Drew
Industrial Division

Ashland Chemical

DAKOTA MINING COMPANY
Gilt Edge Mine

PROGRESS REVIEW
July 1995

Prepared by:
MIKE ETCHINGHAM, ACCOUNT MANAGER
ASHLAND CHEMICAL COMPANY
DREW INDUSTRIAL DIVISION

Ashland Chemical

Drew Industrial Division

Ashland Chemical Company
Division of
Ashland Oil, Inc.

Address Reply:
6842 S. Tucson Blvd.
Tucson, Arizona 85706
Tel.: (602) 294-5522
Fax: (602) 294-5125

July 12, 1995

Mr. Jim Thompson
DAKOTA MINING COMPANY
Gilt Edge Mine
P.O. Box 485
Deadwood, SD 57732

Dear Jim:

Please find enclosed a review of my activities and recommendations at the mine. Included in the progress report are a listing of service visits, activities at the mine, and future projects.

The cooperation of the staff at the mine has been excellent. Together we have been able to control scale in the leach operation.

Thank you for your continued confidence in our services and products. We look forward to continuing to be of service to you.

Sincerely,

Mike Etchingham
Account Manager

ASHLAND CHEMICAL COMPANY
DREW INDUSTRIAL DIVISION

ME:fb

Enclosure

I. SERVICE VISITS

I visited the mine on a monthly basis. At each visit I typically analyzed the leach solutions and determined their scaling tendency. Based on this analysis, I then recommend an appropriate dosage of Millsperse 830® Antiscalant. Any concerns or inadequacies in the treatment program are brought to your attention. I review the feed rates with the operators.

II. ACTIVITIES AND PROJECTS

We have been using Millsperse 830 for the past two years. This product has performed well. Millsperse 830 is a cost effective antiscalant.

The dosage of Millsperse 830 in the leach solutions has been at 7-9 ppm. The leach solutions have not experienced any scale. Some scale was noted in the neutralization circuit and therefore this dosage was increased slightly. The control of the feeding of the antiscalant has been excellent. The operators are keeping this feed rate in prescribed ranges.

We added an antiscalant feed point to the neutralization sump at the heap. There had been scale on the pump in this sump. Therefore, antiscalant was needed at this location.

Drewgard® 315 Corrosion Inhibitor and catalyzed sulfite were added to the heaters at the neutralization building. There had been significant corrosion on the tubes in the heaters. Drewgard 315 will provide corrosion control by passivating the iron surface with molybdate. The sulfite will remove oxygen which causes pitting corrosion.

Drewfloc® 2410 Cationic Flocculant was found to effectively settle the metal hydroxides. This product has been used in the treatment of the water in the pit. It will be used in the new water treatment plant.

III. FUTURE PROJECTS

As the new sulfide ore is introduced to the system, we will monitor the scaling tendency for calcium sulfate. Millsperse 830 is effective in controlling calcite and somewhat effective with the control of gypsum. If the primary scale is gypsum then we will discuss the use of an antiscalant that is primarily effective in controlling this type of scale. This will be dictated by the calcium, alkalinity, and sulfate concentrations in the leach solutions.

IV. CONCLUSIONS

The scale control at the mine has been excellent. The leach water continues to have a severe scaling tendency. Millsperse 830 has been performing well.

The cooperation of the staff at the mine has been excellent. Thank you for your continued confidence in our products and services.

Circulation

1. Alan
2. Robby
3. Martin

NEWMONT METALLURGICAL SERVICES
A DIVISION OF
NEWMONT EXPLORATION LIMITED
417 WAKARA WAY, SUITE 210
SALT LAKE CITY, UTAH 84108

TELEPHONE
(801) 583-6974
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(801) 583-8923

K. MARC LE VIER
DIRECTOR

October 29, 1993

For Town Info & Comments
MP.
11/1/93.

Dakota Mining
410 Seventeenth Street, Suite 2450
Denver, CO 80202

Attn: Mr. Martin Quick
Vice President, Operations

Dear Martin,

Please find enclosed the microbiology report by Jim Brierley as discussed earlier. Please feel free to call either Jim or myself if you have any questions.

Sincerely,

K. Marc Le Vier
Director

KML/wc

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NEWMONT METALLURGICAL SERVICES
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BIOLOGICAL DEPARTMENT

MEMORANDUM

July 12, 1993

TO: [redacted]

FROM: J. A. Brierley

SUBJECT: MICROBIOLOGY REVIEW OF THE GILT EDGE GOLD DEPOSIT, BLACK HILLS, SOUTH DAKOTA

Summary: The Gilt Edge Mine has leach grade (0.046 oz Au/ton) refractory ore. Only 41.3% gold was extracted by direct cyanidation. The high sulfide-sulfur content, 3.50%, suggested the gold may be locked in the sulfide minerals. Diagnostic testing indicated the locked gold was not in the sulfide, rather the refractory gold may be either silica locked or associated with silver. Based on the diagnostic testing, biooxidation would not be an effective process for pretreatment to enhance recovery of the gold.

Acidophilic iron-oxidizing bacteria, such as *Thiobacillus ferrooxidans*, were cultured from a sample of acid rock drainage emanating from a waste rock pile. Given the high sulfide content of the ore, negligible neutralization capacity and the facility with which the bacteria grow on the ore, acid drainage problems are to be expected. Unfortunately, testing to date indicates no beneficial aspects of biooxidation of the ore.

INTRODUCTION

The Gild Edge Mine was toured May 20, 1993 to evaluate potential for microbiological pretreatment of refractory sulfidic ore. Biooxidation of sulfides is evident in a waste dump which produces acid rock drainage. The acidic drainage was sampled to demonstrate the presence of acidophilic iron-oxidizing bacteria. Samples of ore were provided by Laura L. Damon (Metallurgist, Brohm Mining Corp.) for analyses and biooxidation testing.

MICROBIOLOGICAL ANALYSIS

Acid drainage collected for microbiological investigation was analyzed upon return to the laboratory. Table I presents results of testing. The characteristics of the solution indicate the occurrence of biooxidation. All of the iron is in the oxidized ferric form. The pH, although not extremely low, is acidic. The solution pH 4.01 suggests possible dilution effects. The relatively low iron concentration can be attributed to possible dilution and the high pH level causing precipitation.

TABLE I Analysis of Gilt Edge Mine Acid Rock Drainage

pH	4.01
Eh	+514 mV
Ferrous iron	0.0 g/l
Ferric iron	0.61 g/l
Total iron	0.61 g/l

Microbiological analysis demonstrated the presence of acidophilic iron-oxidizing bacteria typical of *Thiobacillus ferrooxidans*.[1] Microscopic observation of the culture bacteria also indicated presence of *Leptospirillum ferrooxidans* like bacteria. No moderately-thermophilic (grown at 50°C) were detected in the sample. The memorandum reporting these results is attached for the record in the Appendix.

Evaluation of microbiological pretreatment of the ore sample is in progress. A stirred-tank reactor with shatter-boxed ore at 10% pulp density has been inoculated with the native iron-oxidizing bacteria. Growth is evident. However, the diagnostic leaching results, discussed below, indicate little beneficial effect for enhanced gold recovery will result from biooxidation of the ore.

ORE CHARACTERISTICS

The sample of ore provided for evaluation represents ore placed on a leach pad for evaluation of direct cyanide leaching. The characteristics of this sample are provided in Table II.[1] The ore is leach grade and refractory with only 41.3% extraction with direct cyanidation. Preg-robbing is not a cause of the low gold extraction. The ore has high sulfide, 3.50%, and low carbonate-C content, 0.05%; based on these values, the net-carbonate-value (NCV) for the ore is -4.61. The ore has high potential for acid generation and essentially no neutralization capacity.

TABLE II Analysis of the Gilt Edge Mine Ore Sample	
Au, Fire Assay	0.046 oz/ton
Au, CN extraction	0.019 oz/ton
Au, CN/FA ratio	41.3%
Au, preg-rob	0.123 oz/ton
S-Total	3.97%
S-Sulfate	0.47%
S-Sulfide	3.50
C-Total	0.06
C-Acid insoluble	0.01
As	0.03
Fe	4.43

Diagnostic testing was conducted to determine why the ore is refractory.[2] Samples were subject to pretreatment by roasting and dissolution in 20% nitric acid to destroy the sulfide matrix. Following the respective treatments cyanide extractions were 0.023 oz Au/ton (50.0% extraction) and 0.022 oz Au/ton (47.8% extraction). The testing indicates the gold is not locked in the sulfide matrix, and biooxidation would not be expected to increase recovery. Pretreatment of the ore with aqua regia resulted in 0.036 oz Au/ton, or 78.3% extraction, indicating possible silica-lock of the gold. Additional testing suggested the refractory gold could also be associated with silver, found present at 0.144 oz/ton. The memorandum reporting the diagnostic leaching results is attached for the record in the Appendix.

JAB/jc

cc: R. Thoreson - Carlin

REFERENCES

1. Hofmann, P. A., "Brohm Mining - Gilt Edge Sample Head Analysis," Memorandum to J. A. Brierley, June 29, 1993.

2. Mc Guire, M. A., "Brohm Mining Head Sample," Memorandum to J. A. Brierley, July 7, 1993.

T. Dugman

Hazen Research, Inc.
4601 Indiana Street • Golden, CO 80403
Tel. (303) 279-4501 • Telex 45-860
Fax (303) 278-1528

March 16, 1994

Mr. Martin Quick
Dakota Mining Company
410 17th Street, Suite 2450
Denver, Colorado 80202

Re: Diagnostic Leaching of a Dakota Mines Gold Ore Sample
HRI Project 006-369

Dear Mr. Quick:

Acting on your behalf, Mr. Herb Osborne requested that we perform a diagnostic leach test on a gold ore sample. The sample was sent to us by a Ms. Laura Damon of Brohm Mining and upon receipt, was assigned HRI Sample Number 47126. The results of the test have already been given to Mr. Osborne; therefore, the purpose of this letter is to provide documentation for your files.

The as-received sample was crushed to ten mesh, and a split was ground for 40 minutes at 50% solids to produce a test charge that was greater than 80% passing 400 mesh. The test (HRI 2155-50) was conducted in five stages.

In the initial stage, the ore was cyanide leached at 30% solids and ambient temperature for 24 hours. The cyanide concentration was adjusted to three grams per liter of solution at the start of the test and was not maintained. Leachable free gold was removed during this cyanidation and amounted to nearly 75% of the available gold.

In Stage 2, the washed cyanide leach residue from the initial cyanidation was repulped and leached with hydrochloric acid solution (HCl) at 50°C to decompose carbonate and iron hydroxide components in the ore. Less than 1.0% additional gold was solubilized in the HCl leach. Once these components had been destroyed and the gold associated with them had been exposed, another cyanidation was conducted. This second cyanidation (Stage 3) was conducted for 24 hours at ambient temperature and at a cyanide strength of three grams of NaCN per liter of solution. Another 5% of the available gold was extracted during this cyanidation. The residue was rinsed in preparation for Stage 4 of the process.

The rinsed residue was repulped and leached in nitric acid solution (HNO_3) at 50°C to decompose the sulfides in the material. The acid leach residue was then washed and subjected to a final cyanidation for 24 hours at ambient temperature and a cyanide concentration of two grams of NaCN per liter of solution. The additional gold extraction achieved by the combined acid leaching and cyanidation was nearly 18%.

Overall, the entire diagnostic leach extracted over 98% of the available gold and all of the available silver values in the sample. The remaining 1.8% of the gold is presumed to be encapsulated in silica. The attached summary provides more details of the test results.

Enclosed is an invoice in the amount of $750 to cover the cost of the test. Should you have any questions or require additional information regarding this test or the enclosed invoice, please do not hesitate to contact John Gathje or me.

Best regards,

Terry L. Dughman
Senior Project Engineer

Enclosure

x.c.: J. Gathje, Hazen

TLD/sm

Summary of Results for Diagnostic Leaching of Dakota Mines Gold Ore Sample

Leach Stage	Test Product	Weight, g or Vol, mls	Assay, oz/st or mg/l		mg		% Distribution	
			Au	Ag	Au	Ag	Au	Ag
CN Leach 1	Filtrate	1680	0.61	1.76	1.025	2.957	74.7	66.0
	Wash	2700	0.08	0.24	0.216	0.648		
HCl Leach	Filtrate	1580	0.007	0.5	0.011	0.790	0.7	14.5
	Wash	3180	<0.007	<0.05				
CN Leach 2	Filtrate	1760	0.03	0.26	0.053	0.458	5.0	11.2
	Wash	3030	0.01	0.05	0.030	0.152		
HNO3 Leach	Filtrate	1710	0.071	0.18	0.121	0.308	11.6	5.6
	Wash	3450	0.021	<0.05	0.072			
CN Leach 3	Filtrate	1620	0.05	0.05	0.081	0.081	6.2	2.7
	Wash	2180	0.01	0.03	0.022	0.065		
	Solids	890.17	0.001	<0.01	0.031		1.8	0.0
Calculated Feed		1000	0.048	0.16	1.662	5.459	100.0	100.0

Overall Distribution of Values:	Gold		Silver	
Baseline Cyanide Leach Solubility =	74.7	%	66.0	%
Iron oxides and/or carbonates =	5.7	%	25.7	%
Sulfides =	17.8	%	8.3	%

DATE: MAY 22, 1995

TO: MARTIN QUICK

FROM: KEITH VAN BUREN

SUBJECT: NATIONAL ELECTRICAL CODE SEMINAR IN SALT LAKE CITY, UTAH

On May 5th and 6th, 1995 I attended the National Electrical Code Seminar, presented by TECO Inc, in Salt Lake City. Mr. Melvin Sanders, who is a member of the National Electrical Code review board, the Institute of Electrical and Electronic Engineers review board, and the National Fire Protection Association board, presented the seminar.

The subjects covered on Friday May 5th were the grounding of power and electronic circuits from the 1993 National Fire Protection Code 79, I.E.E.E. Standard, and the National Electrical Code. Conductor sizing, motor protection, and transformer sizing and protection were also covered. In the afternoon, a workshop on the designing of industrial power systems was conducted.

Material covered on Saturday, May 6th, included selected changes in the 1993 regulations, but dealt primarily with the proposed changes in the 1996 code. Most of the new proposals deal with energy management and the grounding of industrial power systems such as ours here at the Gilt Edge Mine.

During the construction of the bio-oxidation test heap in 1994 at the Gilt Edge Mine, I contacted the I.E.E.E. regarding the grounding of the electrical system on the test heap. Since the heap was to be built upon our existing leach pad, which is isolated from earth by its liner system, a difference in grounding impedance was a problem. The engineers with the I.E.E.E. were very interested in the project as there was nothing in the regulations regarding such a situation.

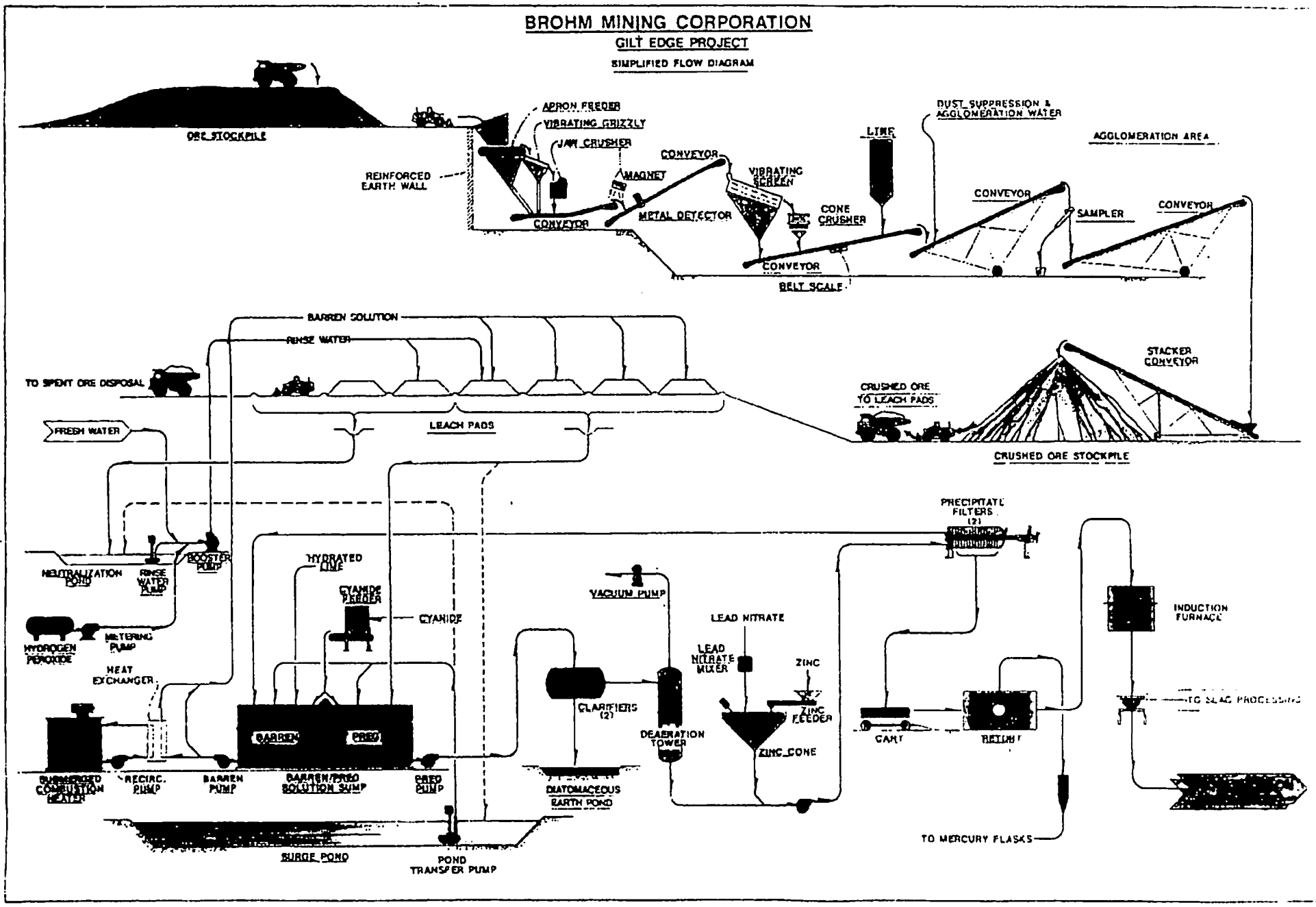
I was asked to make a presentation, during the Salt Lake seminar, on the grounding system I designed for the test heap and for our leach pad. I presented drawings of the bio-oxidation test, drawings of our leach pad construction, photographs of the mine site and leach pad area, and ground impedance test procedures and results used on the pad grounding system. The information was very well received and will be reviewed and used by the I.E.E.E. in the new regulations being adopted for industrial sites such as ours. I have been asked to review the new regulations and procedures before they are adopted and to conduct a tour of our mine site for the panel members this summer.

I received 16 hours continuing education credit for my masters license while attending the conference.

BROHM MINING CORPORATION

GILT EDGE PROJECT

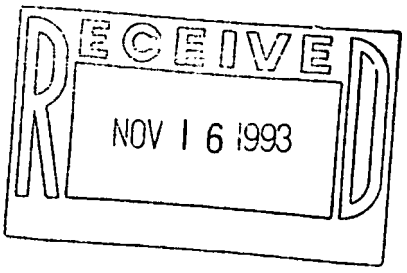
SIMPLIFIED FLOW DIAGRAM



CHAMBERLIN & ASSOCIATES
7463 West Otero Place
Littleton, Colorado 80123
(303) 979-6753

Paul D. Chamberlin
Mineral Processing

This letter is in the Degerstrom Results file.



November 13, 1993

Mr. Martin Quick
Dakota Mining Corporation
410 17th St., #2450
Denver, CO 80202

Re: Gilt Edge

Dear Mr. Quick:

Several questions were raised during our meeting of 11/5/93; some of the answers are enclosed.

The screen analysis of the Polysius core sample is enclosed along with information about the source of the sample. The Polysius report and my followup questions about the report are also enclosed. Figure 3 of the report shows that the crush size was 80% -12 mesh at a roll pressure of 250 MPa and it was 80% -5 mesh at a roll pressure of 155 MPa. We mixed the two crushed samples for the Degerstrom testwork so the average would be 80% -6 mesh

The photos are my only copy (haven't found the negatives) so Laura should keep these for inclusion in her final report.

The only mineralogy reports in my files are enclosed. Fine gold encapsulated in sulfides and silica was seen. Most of the encapsulated gold was in the sulfides.

I looked through my files on bio systems and found nothing about Geobiotics.

I have not yet evaluated the maximum throughput of the present crushing circuit at 100% -1/2" crush size. I will do this after I return from Michigan, about 11/25/93.

Sincerely,

P D Chamberlin

Enclosures

RUSSELL M. HONEA
Consulting Geologist

AC 303 466-8778

Office
1105 BELLAIRE
BROOMFIELD, COLORADO 80020

Mailing Address
P.O. BOX 383
BROOMFIELD, COLORADO 80020

December 3, 1987

Randy Barnes
Minproc (U.S.A.) Inc.
Suite C300
5600 S. Quebec St.
Englewood, CO 80111

Re: Gilt Edge Project
Agreement Nos D-845J-0004

Dear Randy:

As per our telephone conversations earlier in the week I have received and examined four composites from the Gilt Edge Project with results as summarized in the accompanying data sheets (Composites 1, 2, 4, and 5). Each composite was examined in polished sections prepared from both a head sample and a panned concentrate. Percentage composition figures are given for the head sample polished section. Photomicrographs are included for each of the samples examined.

Native gold is present in the panned concentrate sections as liberated particles, as composites with pyrite in which gold is exposed at grain margins, and as smaller locked or encapsulated grains in dominant pyrite from the sulfide suite. Grain size of observed particles varies from 5 to 55 microns. Other sulfides accompanying the dominant pyrite (approximately 95% of total sulfides) include marcasite, chalcopyrite, arsenopyrite, sphalerite, pyrrhotite, galena, chalcocite, and covellite. The latter two copper sulfides are formed as localized concentrations from secondary enrichment related to a redox interface. All of the samples show some oxidation of sulfides to goethite, with Composite-4 being the most strongly oxidized. In this sample goethite at times forms composites with covellite-chalcocite.

The "as received" samples were ground to minus 70 mesh before panning and polished section preparation. In the minus 70 mesh material liberation of sulfides is in the range between 90% and 95%, implying relatively coarse sulfides in the ore suite. Marcasite is finest grained of the sulfide minerals. Most of the sphalerite and pyrrhotite occur as locked grains in pyrite, and chalcopyrite is present as

liberated fragments, as smaller grains locked in pyrite, and rarely as remnants locked in the interiors of chalcocite-covellite aggregates.

Hematite and magnetite are present as remnants from the minor accessory suite of the host rock - as are minor quantities of rutile, zircon, monazite, and garnet.

Please let me know if there are questions or problems regarding either the data or above summary.

Sincerely,

Russell M. Honea

Encl.

RUSSELL M. HONEA
Consulting Geologist

AC 303 466-8778

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Mailing Address
P.O. BOX 383
BROOMFIELD, COLORADO 80020

February 3, 1988

Randy Barnes
Minproc (U.S.A.), Inc.
Suite C300
5600 S. Quebec Street
Englewood, Colorado 80111

Re: Gilt Edge Project

Dear Randy:

Enclosed are results of scanning electron microscope (SEM) examination of two samples (1107 Composite 2 - Panned Concentrate, and Composite 1 - Rougher Concentrate) of concentrates prepared from Gilt Edge ore composites. The data were gathered from three polished sections - two of the Composite 2 sample and one of the Composite 1 sample.

Compositional scans are included for a number of the grains for which scanning electron microscope images were prepared. The six grains of native gold for which compositions were determined show a range from Au-97.60%, Ag-2.40% to Au-82.15%, Ag-17.85%. Average composition of the gold particles is Au-89.42%, Ag-10.58%. "Long count" determinations of both pyrite and marcasite in the samples fails to show any trace of gold in the iron disulfide mineral structure. On the other hand, a "long count" determination of galena indicates the presence of minor amounts of silver in the lead sulfide mineral structure - a conclusion previously suggested on the basis of ammonium dichromate geochemical tests of galena exposed in the polished sections.

Scanning electron microscope data show that scheelite (calcium tunstate) is the carrier for the minor tungsten reported in your chemical determinations. The previously recognized "unknown sulfosalt" mineral is shown by the present data to be the rare lead-bismuth-sulfide mineral lillianite. This is more a mineralogic curiosity than anything else.

Optical descriptions of the Composite 2 (and other core-derived composites) will be supplied soon. These will contain the descriptive detail (including size of gold grains) to go along with the SEM data

Please let me know if there are questions regarding the data. My own feeling at this stage is that we have pretty compelling evidence showing the occurrence of gold in both liberated and encapsulated or locked particles (in both sulfides and silicate gangue). The locked particles are usually smaller than those that are liberated, and it is difficult to estimate with any precision the relative proportions of gold present in each occurrence.

Sincerely,

Encl.

Russell M. Honea

Fine grind (−500 mesh) and leach studies suggest 15-20% of Au is encapsulated.

SUMMARY OF SCANNING ELECTRON MICROSCOPE DATA

GILT EDGE PROJECT, SOUTH DAKOTA

No. 1. 1107 Composite 2 (Panned Concentrate)

Native gold (locked) - Au-97.60%, Ag-2.40%
Pyrite

No. 2 1107 Composite 2 (Panned Concentrate)

Pyrite
Marcasite - no indication of Au in structure.
Chalcopyrite - no indication of gold in structure.

No. 3 1107 Composite 2 (Panned Concentrate)

Native gold (liberated) - Au-84.08%, Ag-15.92%
Pyrite

No. 4 1107 Composite 2 (Panned Concentrate)

Lillianite - $Pb_3Bi_2S_6$ with iron oxide
Pyrite

No. 5 1107 Composite 2 (Panned Concentrate)

Native gold (liberated) - Au-82.15%, Ag-17.85%
Pyrite

No. 6 1107 Composite 2 (Panned Concentrate)

Native gold (liberated) - Au-89.05%, Ag-10.95%
Pyrite

No. 7 1107 Composite 2 (Panned Concentrate)

Native gold (liberated) - Au-89.05%, Ag-10.95% with small inclusions of pyrite
Pyrite
Marcasite
Sphalerite

No. 8 1107 Composite 2 (Panned Concentrate)

Native gold (liberated) - Au-94.57%, Ag-5.43%
Pyrite - no indication of gold in structure.

Phase II, Met. Test Report #1
by Minprec 4/28/88

SECTION V

5.0 MINERALOGY

Mineralogical investigations were carried out on each of the diamond drill core composited rock types. The guidelines followed were those outlined in the Work Order Request to Russ Honea shown in Appendix B. The detailed mineralogical reports submitted by Russ Honea detailing all Phase II mineralogical work are attached in Appendix C.

The objectives of the mineralogical investigations of Phase II were to:

1) Compare the mineralogy of diamond drill core to that of the rotary drill cuttings of Phase I.

2) Confirm the occurrence of gold in the composites mineralization.

3) Identify the occurrence of silver in the drill core composites mineralization.

The mineralogical examination of the diamond drill core composites showed that the mineralogy of the core agrees quite well with the previously reported information on the rotary cuttings. That is, the composite samples examined contained free liberated gold as well as very finely dispersed gold surrounded or encapsulated by mainly sulfides but with some silicate gangue locking and encapsulation. The range in size of gold particles seen in the core composites varies from 3 to 144 microns with an average of 57 microns. The locked or encapsulated gold particles are usually smaller than those that are liberated and no reasonable estimate could be made of the relative proportions of gold present in each occurrence.

Silver was found to be occurring in the following order of abundance:

1) Within the structure of the galena mineral

2) Within native gold in varying amounts

3) Occurring in minor amounts in tetrahedrite-tennantite.

The above mentioned occurrence of silver is most likely the reason for the silver recovery variability in the test work.

A large particle of gold was found in the leach residue of a bulk sulfide flotation concentrate. The particle should have been leached but was not. It was suspected that slow dissolution rates might be

occurring due to the fact that some of the gold could be occurring as electrum. Therefore, compositional scans were conducted on three polished sections, two of Composite #2 and one of Composite #1, for which scanning electron microscope images were prepared. The six grains of native gold for which scans were performed showed a range of gold to silver from Au - 97.60%, Ag - 2.40% to Au - 82.15%, Ag - 17.85%. The average composition of the six particles was Au - 89.42%, Ag - 10.58%. These ratios of gold to silver are not high enough to result in slow dissolution rates.

SEM scans were also performed on both the sulfide minerals pyrite and marcasite to determine if there was gold contained within the minerals structure. The scans failed to show any trace of gold in the mineral structures.

In conclusion the gold in the core composites occurs as free gold and finely dispersed locked or encapsulated gold with the majority being locked with sulfides but some being locked with silicate gangue.

Circulation

1) Alan
2) ~~Robby~~
3) ~~Martin~~.

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NEWMONT EXPLORATION LIMITED
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K. MARC LE VIER
DIRECTOR

October 29, 1993

For Your Info & Comments

MP.
11/1/93.

Dakota Mining
410 Seventeenth Street, Suite 2450
Denver, CO 80202

Attn: Mr. Martin Quick
Vice President, Operations

Dear Martin,

Please find enclosed the microbiology report by Jim Brierley as discussed earlier. Please feel free to call either Jim or myself if you have any questions.

Sincerely,

K. Marc Le Vier
Director

KML/wc

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NEWMONT METALLURGICAL SERVICES
A DIVISION OF
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BIOLOGICAL DEPARTMENT

MEMORANDUM

July 12, 1993

TO: [redacted]

FROM: J. A. Brierley

SUBJECT: MICROBIOLOGY REVIEW OF THE GILT EDGE GOLD DEPOSIT, BLACK HILLS, SOUTH DAKOTA

Summary: The Gilt Edge Mine has leach grade (0.046 oz Au/ton) refractory ore. Only 41.3% gold was extracted by direct cyanidation. The high sulfide-sulfur content, 3.50%, suggested the gold may be locked in the sulfide minerals. Diagnostic testing indicated the locked gold was not in the sulfide, rather the refractory gold may be either silica locked or associated with silver. Based on the diagnostic testing, biooxidation would not be an effective process for pretreatment to enhance recovery of the gold.

Acidophilic iron-oxidizing bacteria, such as *Thiobacillus ferrooxidans*, were cultured from a sample of acid rock drainage emanating from a waste rock pile. Given the high sulfide content of the ore, negligible neutralization capacity and the facility with which the bacteria grow on the ore, acid drainage problems are to be expected. Unfortunately, testing to date indicates no beneficial aspects of biooxidation of the ore.

INTRODUCTION

The Gild Edge Mine was toured May 20, 1993 to evaluate potential for microbiological pretreatment of refractory sulfidic ore. Biooxidation of sulfides is evident in a waste dump which produces acid rock drainage. The acidic drainage was sampled to demonstrate the presence of acidophilic iron-oxidizing bacteria. Samples of ore were provided by Laura L. Damon (Metallurgist, Brohm Mining Corp.) for analyses and biooxidation testing.

MICROBIOLOGICAL ANALYSIS

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TABLE I Analysis of Gilt Edge Mine Acid Rock Drainage

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Ferrous iron	0.0 g/l
Ferric iron	0.61 g/l
Total iron	0.61 g/l

Microbiological analysis demonstrated the presence of acidophilic iron-oxidizing bacteria typical of *Thiobacillus ferrooxidans.*[1] Microscopic observation of the culture bacteria also indicated presence of *Leptospirillum ferrooxidans* like bacteria. No moderately-thermophilic (grown at 50°C) were detected in the sample. The memorandum reporting these results is attached for the record in the Appendix.

Evaluation of microbiological pretreatment of the ore sample is in progress. A stirred-tank reactor with shatter-boxed ore at 10% pulp density has been inoculated with the native iron-oxidizing bacteria. Growth is evident. However, the diagnostic leaching results, discussed below, indicate little beneficial effect for enhanced gold recovery will result from biooxidation of the ore.

ORE CHARACTERISTICS

The sample of ore provided for evaluation represents ore placed on a leach pad for evaluation of direct cyanide leaching. The characteristics of this sample are provided in Table II.[1] The ore is leach grade and refractory with only 41.3% extraction with direct cyanidation. Preg-robbing is not a cause of the low gold extraction. The ore has high sulfide, 3.50%, and low carbonate-C content, 0.05%; based on these values, the net-carbonate-value (NCV) for the ore is -4.61. The ore has high potential for acid generation and essentially no neutralization capacity.

TABLE II Analysis of the Gilt Edge Mine Ore Sample	
Au, Fire Assay	0.046 oz/ton
Au, CN extraction	0.019 oz/ton
Au, CN/FA ratio	41.3%
Au, preg-rob	0.123 oz/ton
S-Total	3.97%
S-Sulfate	0.47%
S-Sulfide	3.50
C-Total	0.06
C-Acid insoluble	0.01
As	0.03
Fe	4.43

Diagnostic testing was conducted to determine why the ore is refractory.[2] Samples were subject to pretreatment by roasting and dissolution in 20% nitric acid to destroy the sulfide matrix. Following the respective treatments cyanide extractions were 0.023 oz Au/ton (50.0% extraction) and 0.022 oz Au/ton (47.8% extraction). The testing indicates the gold is not locked in the sulfide matrix, and biooxidation would not be expected to increase recovery. Pretreatment of the ore with aqua regia resulted in 0.036 oz Au/ton, or 78.3% extraction, indicating possible silica-lock of the gold. Additional testing suggested the refractory gold could also be associated with silver, found present at 0.144 oz/ton. The memorandum reporting the diagnostic leaching results is attached for the record in the Appendix.

JAB/jc

cc: R. Thoreson - Carlin

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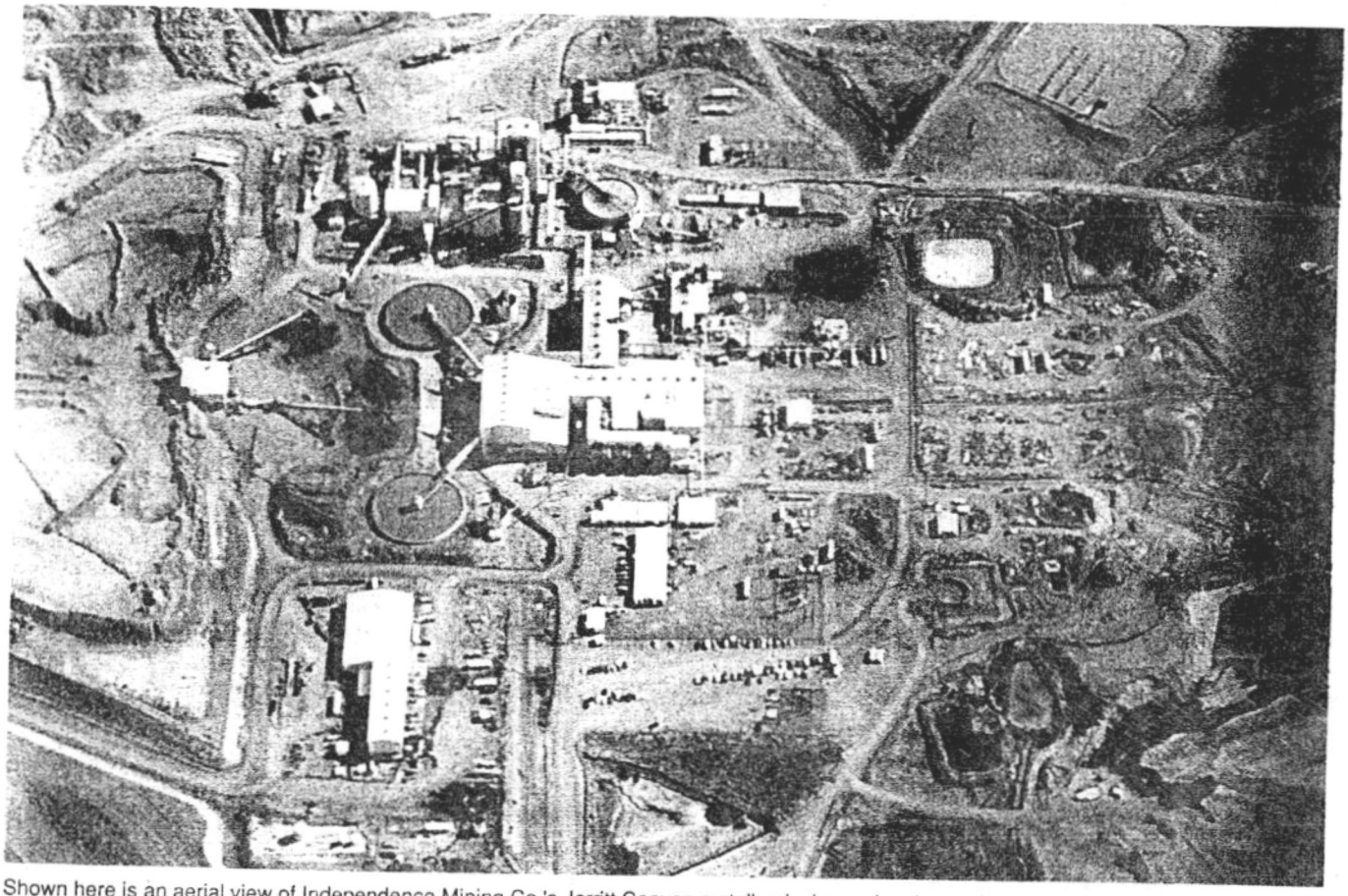
1. Hofmann, P. A., "Brohm Mining - Gilt Edge Sample Head Analysis," Memorandum to J. A. Brierley, June 29, 1993.

2. Mc Guire, M. A., "Brohm Mining Head Sample," Memorandum to J. A. Brierley, July 7, 1993.

Oxygen roasting of refractory gold ores

Michael Brittan

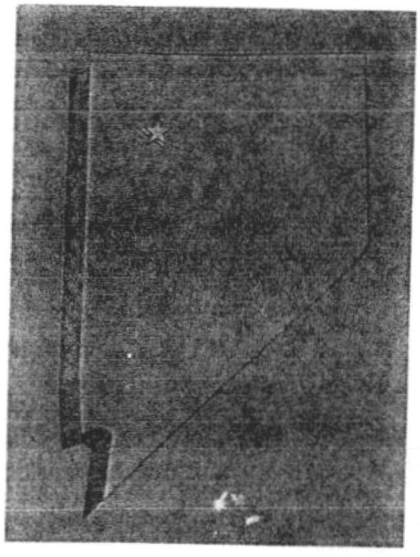


Shown here is an aerial view of Independence Mining Co.'s Jerritt Canyon metallurgical complex, located north of Elko, NV.

For several years, Independence Mining Co. (IMC) has routinely used oxygen fluid-bed roasting to pre-oxidize refractory gold ores ahead of conventional carbon-in-leach (CIL) processing. Oxygen serves jointly as the fluidizing medium and the combustion gas. This technology has proven to be reliable, environmentally sound and cost-effective.

IMC is a subsidiary of the Minorco group. The company operates the Jerritt Canyon (a joint venture with FMC Gold) and Big Springs gold mines in the Independence mountain range north of Elko, NV.

Ore bodies in the range contain characteristic refractory ore. It requires pre-oxidation ahead of conventional CIL processing. This article describes the technology developed specifically to treat these difficult ores.



Location map of Independence Mining's Jerritt Canyon gold operation

Native gold generally occurs disseminated as micron- to submicron-sized inclusions intergrown with, or encapsulated in, pyrite, goethite oxidation pseudomorphs of pyrite, and quartz or silicate gangue. Aside from the dominant pyrite, lesser sulfides present are arsenopyrite, marcasite, stibnite and realgar. The ores also contain microfine organic carbon and photographite. The gangue is dominated by silicates containing barite and the carbonates calcite and dolomite. Minor gangue minerals include zircon, rutile, ilmenite and magnetite.

Michael Brittan is Consulting Metallurgical Engineer, Independence Mining Co., Inc., 5251 DTC Parkway, Suite 700, Englewood, CO 80111. Brittan presented the paper on which this article is based at the Northwest Mining Association Meeting, Nov. 29-Dec. 2, 1994, in Spokane, WA.

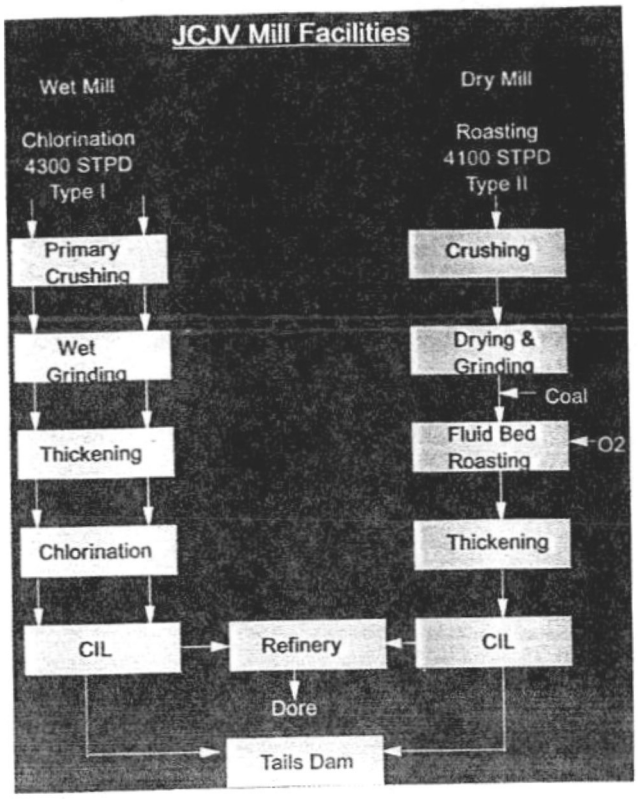


Fig. 1

Refractory characteristics

Jerritt Canyon ores are refractory on two counts. First, gold particles that may be free or only partially occluded will be amenable to reaction with cyanide and oxygen in classic leaching fashion. However, the gold-cyanide complex will immediately be adsorbed from the solution by the organic carbon, which is highly active. Due to the intimate association of the gold and carbon in the ore, this preg-robbing overrides gold recovery on activated charcoal added in a conventional CIL circuit.

Second, gold particles occluded in pyrite are effectively screened from contact with cyanide in solution. Big Springs ores tend to be higher in pyrite and lower in carbon than those at Jerritt Canyon.

Destruction of the pyrite matrix by oxidation and passivation of the active sites on the native carbon are required to extract the gold. The gold locked in quartz or silicates is not liberated at practical grinds in a mill and may, therefore, be considered as true unrecoverable tails.

Processing options

Processing options for Jerritt Canyon-type ores are limited to pre-oxidation methods that can destroy the sulfides as well as the activity of the native carbon. Acidic autoclaving is precluded because of the basicity of the ores (which will incur high acid consumption) and the inability of pressure oxidation to passivate the organic carbon, except under very stringent and costly conditions of temperature and pressure. Alkaline autoclave oxidation, even under extreme conditions, has not been able to generate adequate gold recovery. Biological or chemical oxidation are similarly limited in their ability to deal with the organic carbon difficulty.

Chlorination has been used effectively since the start-up of Jerritt Canyon in 1981. Chlorine serves a dual function of oxidizing the sulfides, thereby liberating the occluded gold, and of passivating the active sites on the carbon particles.

However, ores in which most of the gold is locked in pyrite tend to be more refractory. These ores require substantial sulfide oxidation to achieve reasonable gold recoveries. The associated chlorine consumption adversely affects process economics, particularly for high-sulfide ores.

Oxygen roasting

A trend toward more refractory ore and higher chlorine prices prompted development of the whole-ore oxygen roasting process. This resulted in the commissioning of facilities at IMC's Big Springs and Jerritt Canyon mines in 1989.

This process solves the refractory problem by combusting the sulfides and organic carbon to virtual completion. This renders the gold amenable to high recovery by conventional cyanidation. Process rights are owned jointly by IMC and Freeport-McMoRan, the original developer of the technology. The history of the developments at Jerritt Canyon and Big Springs is described in the literature.

Roasting ore in fluidized bed reactors (an outgrowth of the fluid-bed catalytic-cracking units used in the petroleum industry) and using oxygen as the fluidizing/combustion gas are key factors embodied in the technology. They provide a process with economic advantages over alternative oxidation methods for relevant ore types in terms of gold recovery efficiency and costs.

Fluid-bed roasting makes for a low capital cost, low maintenance operation with effective process control. It is well-suited to roasting IMC ores due to the exothermic combustion of the natural fuel inherent in the ore's sulfide and carbon components.

Use of pure oxygen avoids nitrogen dilution. This substantially reduces the size (and hence the capital cost) of the equipment. And it provides a more favorable chemical reaction regime. By fixing sulfide oxidation products and elements such as arsenic in the solid phase, the system is also environmentally attractive.

Current facilities

The chlorination and roasting processes currently operate side-by-side at Jerritt Canyon (Fig. 1). Each treats more than 3.6 kt/d (4000 stpd) of ore. Chlorination is used to pre-oxidize less refractory ores. Roasting is used for the more refractory varieties.

The Jerritt Canyon roasting circuit was installed in 1989 at a capital cost of $55 million. This included crushing, grinding, twin roasters, off-gas handling, quenching, thickening, CIL and carbon elution. It did not include the oxygen plant. On a stand-alone basis, the operating cost from primary crushing through tails disposal is less than $16.50/t ($15/st).

The complete 1.1-kt/d (1200-stpd) Big Springs facility, including the tailings dam but excluding the oxygen plant, cost $26 million. This plant is now shut down due to depletion of the mine's ore reserve.

Crushing and grinding circuit

The Jerritt Canyon mill that feeds the roasters operates on a dry basis through crushing and grinding. This avoids expending fuel to vaporize and raise to roasting temperature water that would otherwise be associated with conventional wet grinding circuits. Water vapor would also add unnecessarily to the gas volumes to be handled in the roasters and the off-gas train. This would increase the size and capital cost of the equipment. Following quenching of the roaster calcine, processing continues in conventional wet slurry form through thickening and CIL. Figure 2 shows Jerritt Canyon's flowsheet.

For a greenfield project, dry grinding works out to be considerably more economical than wet grinding followed by filtration and drying of the cake.

Ore from the primary crusher stockpile (-127 mm or -5 in.) is reduced to -13 mm (-0.5 in.) in two stages of crushing. This consists of one standard and two Shorthead (1.3 m or 4.25 ft) Symons cone crushers. A rotary dryer is inserted between the second and third crushing stages to ensure reduction of ore moisture levels to less than 1%. Drying at this point avoids potential material handling problems that could arise from the screening and conveying of wet ore at a finer size.

The dry grinding system is an adaptation of that used in the cement industry. But it is designed to generate a 106-µm (150-mesh) product rather than the 45- to 38-µm (325- to 400-mesh) typical of cement.

Grinding is done in a 4.5- x 5.6-m-diam (14.5- x 18.5-ft-diam), 1.8 MW (2500 hp) Fuller grate discharge ball mill. The grinding-induced temperature is about 82° C (180° F), which, in conjunction with an air sweep in the mill, results in further ore drying.

A combination of air slides and bucket elevators transport the ore in the dry grinding circuit. Classification by a Fuller O'SEPA classifier (the analog of a cyclone in a wet grinding system) returns coarse underflow to the mill and passes the final product to dry cyclones backed up with a baghouse for fine dust recovery.

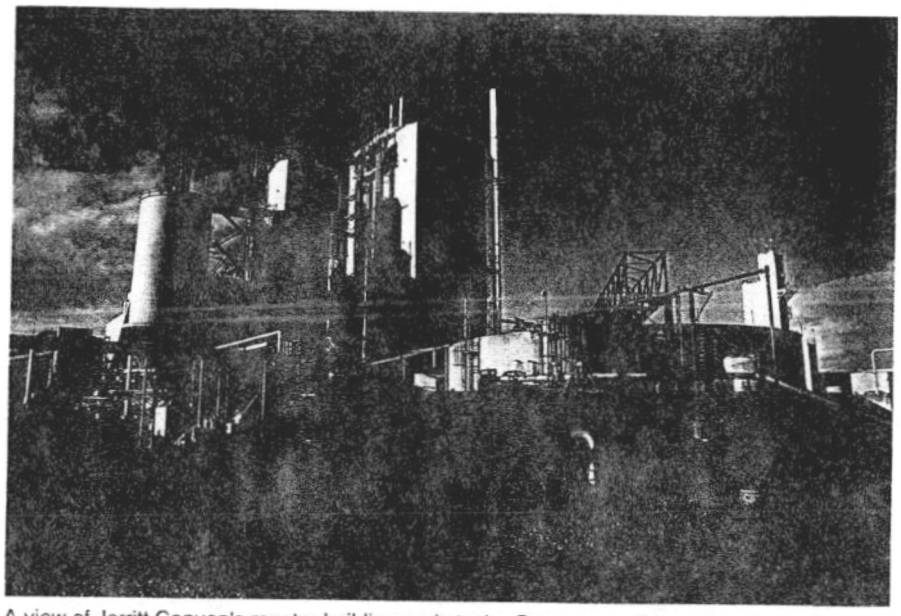
A 1.8-kt (2000-st) roaster feed bin stores the comminuted product. It averages a size distribution of about 5% +250 µm (+65 mesh) and 50% -75 µm (-200 mesh).

Roasting and off-gas handling

The roasting system at Jerritt Canyon is comprised of two parallel, two-stage, fluid-bed roasters designed by Dorr-Oliver. Oxygen serves a combined function as combustion and fluidizing gas.

As shown in Fig. 2, a variable speed screw in combination with a rotary air lock withdraws ore from the roaster feed bin. Coal is added as fuel to supplement the inherent sulfide-carbon fuel content of the ore. This allows attainment of autothermal roaster operation and temperature control.

A bucket elevator conveys the feed to the top of the roasters. There the feed system adds the material to the top (first) stage of each roaster. As shown in Fig. 3, the ore drops from the first stage to the lower second stage from which it is discharged to the quench system. The ore moves countercurrent to the fluidizing oxygen fed by a windbox to the second (lower) stage fluid bed. All ore and gas transfers are external to the equipment. This aids access without having to shut down and enter the roasters.



A view of Jerritt Canyon's roaster building and stack. Oxygen roasting at the plant solves the refractory problem by combusting the sulfides and organic carbon to virtual completion. This renders the gold amenable to high recovery by conventional cyanidation methods.

Roaster exit gas traverses several scrubbing stages for particulates, sulfur dioxide and mercury.

Ore mineralogy and atmospheric discharge regulations dictate the gas cleaning requirements. The quenched calcine is thickened and then fed to a standard CIL circuit for gold extraction. Gold recoveries are functions of ore grade and mineralogy, but routinely exceed 90%.

Advantages of the IMC system

The fluid-bed roasting system is simple with no moving parts. High availabilities are achieved. It is effective as a gas-solids contactor. This fosters excellent mixing, efficient heat transfer and therefore uniform temperature, an important feature ensuring high gold recovery efficiency.

Starting and stopping the roasters is straightforward, making operation and maintenance easier.

The use of oxygen as opposed to air as the fluidizing-combustion gas reduces the size and capital cost of the roasters since they do not have to accommodate the inert nitrogen flow. Similarly, the off-gas train is also smaller than would be the case with an air system due to the

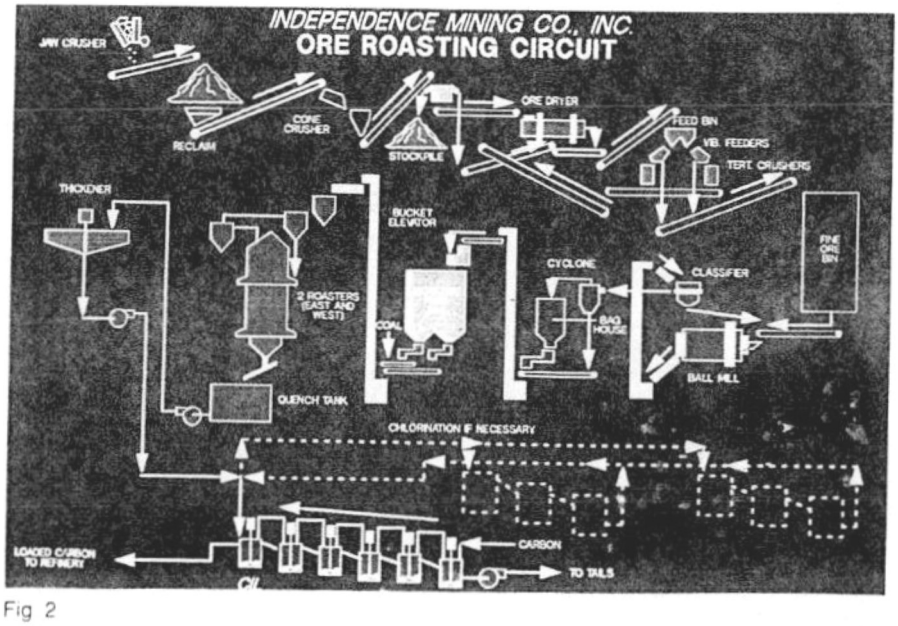


Fig 2

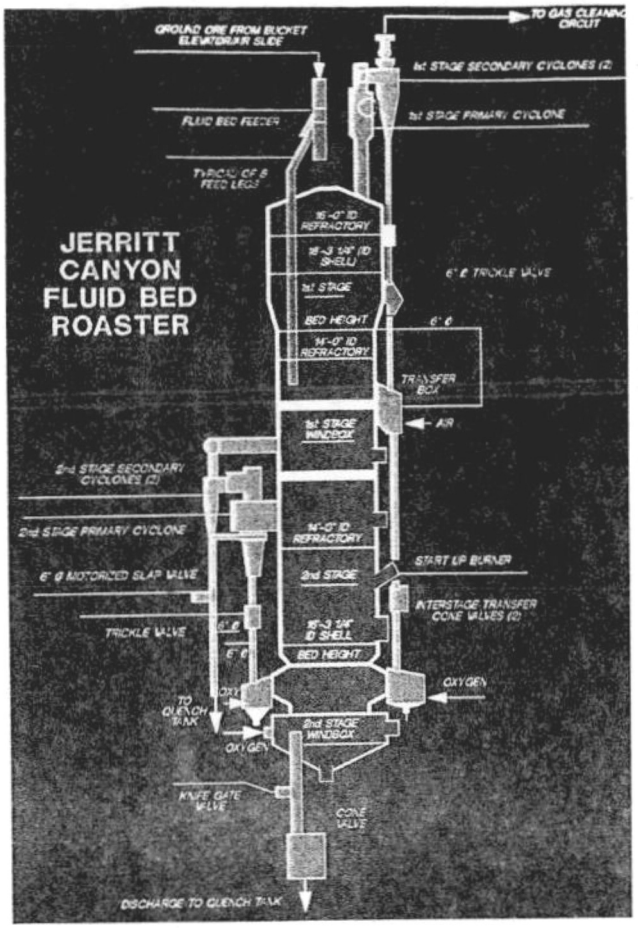


Fig. 3

low gas volumes in the absence of nitrogen dilution. It has been estimated that a single 4.3-m-diam (14-ft-diam) oxygen roaster can treat the same ore throughput as two 7.3-m-diam (24-ft-diam) air roasters.

The absence of nitrogen also enhances the energy efficiency. There is no nitrogen to be raised to combustion temperature, thereby reducing auxiliary fuel requirements. This nitrogen would transport heat out of the system in the off-gas. The waste energy would be lost or would require costly, maintenance-intensive heat recovery equipment.

Use of pure oxygen also achieves high conversions of sulfides and carbon at lower combustion temperatures than traditional air roasting. This improves gold recovery, lowers supplemental fuel requirements and reduces heat losses from the system.

The two-stage, countercurrent scheme promotes combustion and energy efficiency. Thus, the incoming oxygen contacts outgoing ore in the lower fluidized stage. This provides a high driving force to complete the combustion of any residual unburned particles, principally the slower-burning carbon, remaining after the first (upper) stage of combustion. This is important since the roasting process will activate any residual carbon particles in the ore rendering them highly preg-robbing. This would adversely effect gold recovery in the downstream CIL train.

The lower fluid bed also preheats the gas stream before it effects the lion's share of the combustion in the upper bed. This is tantamount to recovery of some heat from the solid phase before it discharges from the reactor.

Quenched roaster calcine yields a low viscosity pulp for CIL. The pulp generated by other pre-oxidation techniques may tend to be viscous, with adverse gold recovery.

The strong oxidizing conditions associated with oxygen make for a favorable chemical reaction environment. Thus, pyrite particles tend to be converted not to dense magnetite, but to porous hematite, which shrinks and cracks and improves cyanide access. Formation of ferric arsenate is promoted, permitting arsenic to be fixed in the solid phase. The presence of calcite and dolomite (supplemented, if necessary, by adding lime or soda ash) permits most of the sulfide gases to be captured in the fluid beds. This leaves only a small fraction to be dealt with by the off-gas scrubbing train.

The system has met or exceeded all of the Nevada environmental requirements. The absence of nitrogen minimizes NO_X emissions. Meanwhile, the strongly oxidizing atmosphere keeps carbon monoxide and unburned hydrocarbons in the exit gas below environmentally acceptable limits without the need for afterburning.

The use of oxygen, as opposed to air, allows use of lower fluidizing velocities. This minimizes solids carryover in the exit gas and promotes more complete oxidation of sulfides and carbon. This is particularly important for the slower-burning carbon.

Roasting temperatures are relatively low, which avoids sintering of the ore. Such slagging at higher temperatures can encapsulate gold particles. This will have a detrimental effect on gold recovery since access by cyanide is hindered or prevented. Fluidized beds are an effective means of controlling high temperature combustion reactions since they provide good temperature uniformity and control.

For sulfide ores without carbon, which could conceivably be treated by alternative pre-oxidation processes, whole-ore oxygen roasting will generally be more economical.

Process requirements

The fuel value of the ore should be in a range that derives maximum benefit from the process. If the inherent fuel content associated with sulfides and carbon is too low, larger additions of supplementary fuel will be required, adding to operating costs. If the fuel value is too high, the roasting process will exceed the autothermal limit, the bed temperatures will rise and gold recovery may decline. This can be counteracted by air or water injection. But some of the advantages of the system may be lost or production may suffer.

Natural ore carbonates may have to be supplemented if they are insufficient to fix an adequate amount of sulfur as sulfate in the solids. If gypsum formation is excessive, it can cause downstream scaling problems in the quench-thickening circuit. Appropriate design and operating steps must be taken.

Potentially noxious, volatile components that cannot be fixed or readily scrubbed from the exit gases could require additional recovery systems.

An oxygen plant is needed, albeit supplying low-pressure oxygen. Autoclaving requires more costly high-pressure oxygen. ♦

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Vern - FYI

HECLA MINING COMPANY

September 6, 1991

MEMORANDUM TO: George Johnson
Todd Fayram

FROM: John Haan JGH

SUBJECT: **Biological Neutralization of Spent Heaps**

Attached is information regarding bio-treatment of cyanide and metal complexes. This information may be of interest in neutralization of both the Cactus and Yellow Pine dedicated heaps. According to information we have received from Pintail, they are discussing neutralization costs in the range of $.03 to $.04 per ton for large heaps. Although this may be optimistic, I feel that we should pursue researching the viability of biological neutralization of our heap leach facilities.

The advantages of biological treatment of heaps may be both long term and short term. Long term advantages may include less risk of residual cyanide drainage from the heaps after snowmelt or rainfall. The short term advantage may be in total cost of neutralization. Pintail believes that biological neutralization is competitive with chemical destruction of cyanide. Another possibility may be to detoxify the cyanide to a certain level using chemical oxidizers and follow up with biological treatment of the heap.

USMX is neutralizing, or planning to neutralize heaps at Alligator Ridge using microbes. Listed below are contacts at Pintail and USMX.

Pintail Systems, Inc.
L. C. Thompson
Director Research & Development
Denver Lab: (303) 367-8443
Corporate Office: (203) 658-2977

USMX
Richard Jolk, P.E.
Chief Metallurgist
(303) 985-4665

JGH/pjh

Attachment

xc: George Wilhelm

INTRODUCTION

to

Pintail Systems, Inc.

Natural Biological Treatment Systems for Problem Industrial Wastes

Who We Are

Pintail Systems, Inc. is a multi-disciplinary company specializing in the development and implementation of innovative biological treatment programs for industrial waste. PSI began operations offering consulting, research and treatment design services to mining, energy and electronics industries. We offer our products and services nationwide.

Our Mission

Pintail Systems, Inc. was founded to develop natural treatment technologies for a broad spectrum of problem industrial wastes. Bacteria isolated from waste sources and augmented for specific contaminant removal offer cost-effective, environmentally acceptable alternatives for organic and inorganic decontamination. The PSI staff includes geologists, engineers, chemists and microbiologists who are dedicated to the development and dissemination of these new remediation technologies.

Specific bioremediation programs offered by Pintail Systems include:

- Biological concentration of metals from waste streams or groundwater
- Bioremediation of phenols
- Bacterial decomposition of alkali or metal cyanide compounds in solid or aqueous wastes
- Denitrification of agricultural or industrial process wastewater
- Bio-decomposition of petroleum-based wastes from spills or manufacturing
- Remineralization of soluble mineral consituents of waste streams

The PSI staff is committed to providing support from site assessment through treatment execution.

Technical Capabilities

Pintail Systems was founded to provide environmental consulting and treatment services for a broad-based industrial clientele. Some of the technical services offered by PSI staff at our laboratory or branch offices include:

Research and Development

- Treatment bacteria isolation and augmentation
- Feasibility Studies
- Bench-scale testing
- Pilot plant design and operation
- Process Analysis

Environmental Services

- Site assessment
- Soil and groundwater sampling
- Sample analysis
- Contaminant characterization
- Treatment program development

Laboratory Services

- Comprehensive biological, chemical and environmental analysis
- Standard water quality testing

Project Management

- Treatment program design
- Cost analysis
- Mobilization/de-mobilization
- Site management
- Treatment analysis
- Remediation assessment
- Mathematical modeling

PINTAIL Systems, Inc.

Technical Report Series

Report G-101

Biotreatment Processes for Industrial Wastes

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PINTAIL Systems, Inc.
Technical Report Series
Report No. G-101

Biotreatment Processes for Industrial Wastes

Abstract

Biotreatment is a new word defining old and natural processes for waste recycling. This review defines biotreatment technology and explores the application of biological treatment processes to a variety of industrial wastes. Microbial treatment techniques have improved during the last decade with advances in biotechnology and bioengineering research. The technical expertise is now available to apply augmented, natural technology to non-traditional operations (Johnson, et al).

Introduction

Since the dawn of civilization, man's metabolic activities have resulted in the production of organic and inorganic wastes. The population explosion during the last century and the Industrial/-Technical Revolutions have caused a dangerous imbalance between man and nature. This imbalance is reflected in a disruption of the global cycling of minerals, metals and various elements. A balanced system is a state of dynamic equilibrium. Biological and geological processes of synthesis, transformation and decomposition continuously take place. The results of man's intervention in nature's cycles include extraction of non-renewable resources and dispersion of wastes in forms that are incompatible with natural recycling processes (Busch). Man has contributed to the destruction of this dynamic equilibrium. He must be responsible for reversing waste disposal philosophies and the resulting pollution.

Bacteria have been used for aqueous waste treatment for over 40 years (Metcalf and Eddy). In a municipal or agricultural waste treatment system, bacteria can degrade many organic wastes to harmless by-products through normal cellular metabolic reactions. These treatment methods use bacteria that naturally exist within the waste removal system. The complexity, concentration and potential high toxicity of industrial wastes, however, often prevent the use of natural bacteria processes. The key to successful biotreatment of industrial pollutants is the discovery and adaptation of bacteria that are tolerant to the waste and able to degrade it biochemically.

Biotreatment is defined as the use of natural or augmented bacterial systems to remove or decompose an undesirable waste in a controlled environment. These processes use bacteria that are either naturally found in the waste or that have been enhanced for treatment in the laboratory and re-applied to the system. Natural treatment processes can be applied in engineered treatment plants or *in situ* for solid waste or soil remediation.

Reversal of pollution requires the elimination of the point sources of contamination, as well as waste renovation and resource reclamation. Recent advances in biotechnology and bioengineering have made all of these goals conceptually possible. Biotreatment technologies offer a well engineered, natural solution to treatment of problem wastes. Augmented natural processes offer industries the chance to have a positive impact on the global environment.

Industrial Pollution - Definition and Source Identification

Pollution is defined as any manufactured, transformed or naturally occurring substance which can have a detrimental effect on man or his environment. The need for pollution control arises from depletion or destruction of resources, as well as the concentration of undesirable contaminants in the environment. Other factors affecting the need for control include the increasing moral and legal obligations for source treatment and the high costs of conventional remediation. Some wastes have a long-term persistence in the environment and in-perpetuity treatments are prohibitively expensive to

the point of affecting the profitability of many key industries. An economical alternative to conventional treatment or disposal options is clearly needed.

Increasing sources of contamination are found in manufacturing, distribution and production use industries as well as mineral extraction, petroleum refining and power generation. Major sources of pollutants include the following examples of a few wastes and their origins:

* Natural Sources - heavy metals, nitrates, asbestos, ash emission (volcanoes, forest fires);
* Transformed Pollutants - sewage, fertilizers, heavy metals, acid wastes;
* Synthetic Toxins - pesticides, manufactured organic intermediates, petrochemicals and surfactants;

The remainder of this review summarizes traditional pollution control technologies and suggests where new approaches apply. How biotreatment processes work for each waste and what treatment levels are attainable in a large-scale operation are included in specific case studies. The treatments for waste generated by the following industries will be considered in review because they represent natural, transformed and synthetic sources of pollutants.

1. Mining/metal finishing industries - wastes generated include metal-cyanide complexes, free cyanide and heavy metals.

2. Pesticide manufacture - wastes generated include pesticide intermediates and cyanides.

3. Paper and pulp manufacture - wastes include phenols, formaldehyde and solids.

Bioremediation of hazardous wastes is a developing technology that will provide accelerated treatment using natural global cycling processes. The basic global cycle is diagrammed in Figure 1.

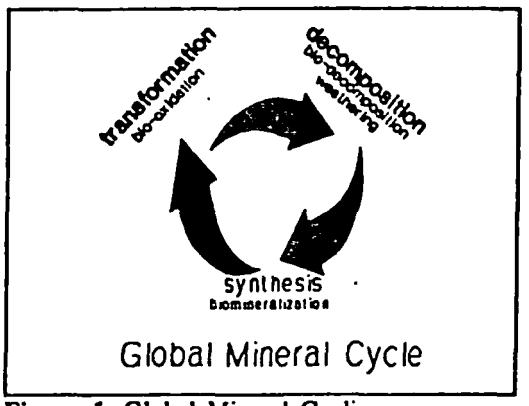

Figure 1. Global Mineral Cycling

Mining and Metal Finishing Wastes

Traditional and Biotreatment Options

Mining and metal manufacturing processes can generate both solid and liquid wastes which contain free cyanide, metal-cyanide compounds and heavy metals. If the wastes are not adequately contained, they can adversely effect surface water, groundwater and soil quality (Towill, et al). The traditional treatment options for these wastes include immobilization, ion exchange, chemical oxidation, precipitation, thermal decomposition or electrical treatment methods (Huiatt, et al). All of these approaches are effective to a degree, but can leave behind secondary problem pollutants, and can be costly. Choice of any pollution mitigation scheme requires the following information:

* What levels of removal must be met;
* Possible environmetal impacts from no treatment or from the treatment process;
* Waste characteristics restricting some treatments;
* Cost of the treatment program;
* Commercial availability of the process.

The following evaluation matrix lists the treatment levels attainable by traditional and biological methods for cyanide removal.

Other methods of cyanide removal that were not reviewed include iron precipitation and electrical treatments. Each treatment has advantages and disadvantages that must be evaluated according to the required mitigation levels and cost factors. Biotreatment processes should be included in any evaluation as the technology is now available for cyanide and metal-cyanide decomposition and removal or immobilization of heavy metals (Thompson and Gerteis). The advantages of biological treatment over many of these traditional processes are

* low comparative treatment costs,
* complete waste treatment and removal,
* recovery of treatment bacteria,
* formation of non-toxic end products,
* de-listing of hazardous wastes constituting an end to liability for the waste.

Table I. Evaluation of methods for cyanide decomposition.

	cyanide complexes removed:			
treatment	free CN	WAD cyanides	ferro cyanides	CNS
1. alkaline chlorination	yes	partial	no	partial
2. ozonation	yes	yes	yes	yes
3. peroxide treatment	yes	partial	partial	no
4. ion exchange	no	yes	yes	possible
5. natural degradation	yes	partial	no	no
6. bio-decomposition	yes	yes	yes	yes

WAD= weak acid dissociable metal cyanide (e.g. copper, zinc, nickel, cadmium cyanides)

Biological degradation of cyanide in gold mining effluents is currently used as an alternative to traditional treatment technologies in both the USA (Mudder and Whitlock) and the Soviet Union (Grableva, et al). Another industrial process is one which degrades free cyanides through enzymatic hydrolysis reactions. These processes are being used on an industrial scale and show the promise of biotreatment for a variety of other cyanide and metal-cyanide wastes.

Collection or immobilization of many heavy metals has been observed in various species of bacteria (Trudinger and Swaine). Biological processes use both live and inert biomass for metal sequestering. These reactions contribute to bacterially mediated mineralization and de-mineralization reactions in nature. Metals are reformed into mineral species by natural precipitation, chelation or complexation reactions (Eccles and Hunt). Processes that ordinarily proceed on a geologic time scale can be accelerated by use of specific bacteria to immobilize free metals in aqueous or solid matrices. Metal contamination in soil can be remediated by adding bacteria which immobilize and re-mineralize soluble metals. One distinct advantage of the biological methods is that they operate at a fraction of the cost of conventional precipitation or filtration methods. The metals are economically recoverable from a biological system which aids in the recycling of non-renewable resources, as well as reduction of treatment costs.

The wastes amenable to biotreatment include

* cyanide wastes produced in mining operations,
* heavy metal-contaminated aqueous and solid waste,
* cyanide-contaminated aluminum pot liners, soil and groundwater,
* toxic ions in soil, vapor and aqueous phases.

Processes that have been demonstrated in the mining industry should also be adaptable to specialized wastes such as electroplating solutions and nitrate or phosphate agricultural wastes.

Pesticide Manufacturing Wastes

Traditional and Biotreatment Options

Wastes from pesticide manufacturing processes include organic process intermediates as well as cyanides and some heavy metals. The short-term persistence of many pesticides in soil is attributed to microbial activity (Prave, et al). Although there is a large difference between concentrations of pesticides found in soil and those found in manufacturing waste streams, many bacteria have the potential to convert complex organic pesticides to harmless, natural by-products. Species of Bacillus, Pseudomonas, Arthrobacter, Achromobacter and Norcardia have all been implicated in the decomposition of pesticides. Research dating back more than 30 years has shown that many bacteria digest complex organic pesticides for use as nutrient sources for microbial life processes (Higgins and Burns). The treatment problem, as with mining wastes, lies in the conversion of natural processes to the scale necessary for industrial application.

Pesticides that have been shown to be susceptible to bacterial decomposition include members of the groups of chlorinated hydrocarbons, organophosphates, carbamates, triazines and pyrethroids. The fundamental mechanisms of decay catalyzed by bacteria include dehalogenation, amide and ester hydrolysis, dealkylation, oxidation and reduction. Applied bacterial treatment systems are engineered through bioaugmentation technology to treat aqueous waste streams and contaminated soil.

Current waste removal technology for pesticide manufacturing involves a combination of recycling technology, solid hazardous waste disposal and incineration. All of these processes are energy and capital-intensive. Biotreatment is not a solution for treatment of all manufacturing waste streams but can influence parts of the overall treatment process with more efficient and economical solutions. Waste streams that could be handled by biotreatment processes include

- cyanides formed as a by-product of pyrethrin manufacture,
- heavy metals from raw material processing,
- organic intermediates that are not recycled,
- trace contaminants in discharge streams.

Biotreatment development for any of these wastes is accomplished by bacteria isolation, adaptation and enhancement followed by laboratory testing, field pilot studies and final treatment process design. Biological treatment of pesticide manufacturing wastes is conceptually possible and is being used in some select applications.

An example of a commercially available process for pesticide waste streams is the biotreatment of free cyanide by-products formed in some manufacturing processes. Current waste treatment technology emphasizes either a chemical oxidation or a complexation/precipitation as an insoluble ferrocyanide. The ferrocyanides are removed and stored as a solid, hazardous waste. The biotreatment alternative would involve a two-stage biological treatment. The first step would use an enzymatic hydrolysis from microbial enzymes to lower ionic cyanide from high concentrations to less than 100 mg/L. The second, polishing step would use an augmented bacteria culture in a suspended growth treatment to reduce cyanide levels to below drinking water standards. The advantage of the biotreatment method would be in cost reduction and removal of liability for a hazardous waste. The engineering design can handle large volumes of waste on either a batch or continuous treatment design.

Paper and Pulp Manufacture

Traditional and Biotreatment Options

Wastes from paper manufacturing processes include solid sludges, phenols, and formaldehyde, among others. Current waste treatment methods have developed integrated biological waste removal systems for many of the problem pollutants. Recent advances in pollution control technology for the paper and pulp industries have supplied economically viable, natural treatment methods which are energy and cost-efficient.

The principle wastes come from the release of pulping and bleaching chemicals. Clarification and biological treatment are used in paper mills in the U.S.A. (Hakulinen, et al) and Canada. The successful operation of biotreatment processes has demonstrated that even strict ecological standards can be met with an economically viable process. Primary effluent treatment is designed to reduce any biodegradable portion of dissolved organic waste. This results in an improvement of both BOD and COD levels in treated water. Secondary and tertiary treatment finishes a polishing step where toxins, gases and dissolved organics are removed through biodegradation processes. Further refinements in treatment methodology should improve the economics and efficiencies of biotreatment processes for the paper and pulp industries.

An example of a process improvement is the recent advance in decomposition of highly toxic phenols by bacteria. Bacteria can be immobilized in a fluidized bed extraction system for aqueous waste streams (Holladay, et al). The microbial treatment system degrades the phenols to harmless by-products with a very short residence time for effluent solutions. Two biotreatment scenarios are illustrated in Figures 2 and 3. A biodecomposition pathway for phenol and naphthalene is diagrammed in Figure 4.

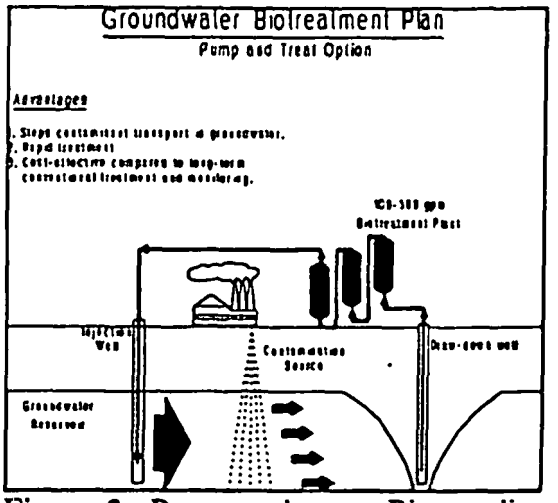

Figure 2. Pump and treat Bioremediation

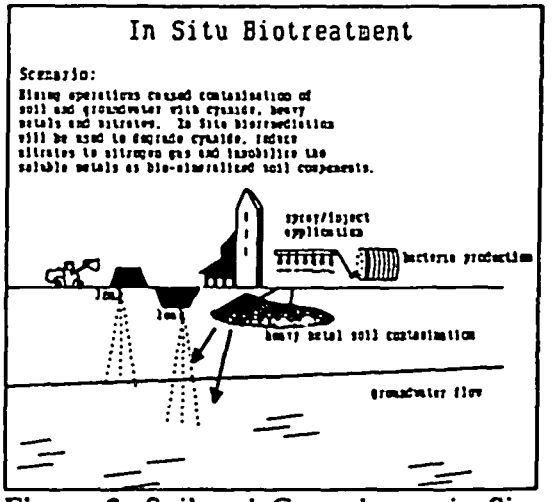

Figure 3. Soil and Groundwater in Situ Bioremediation

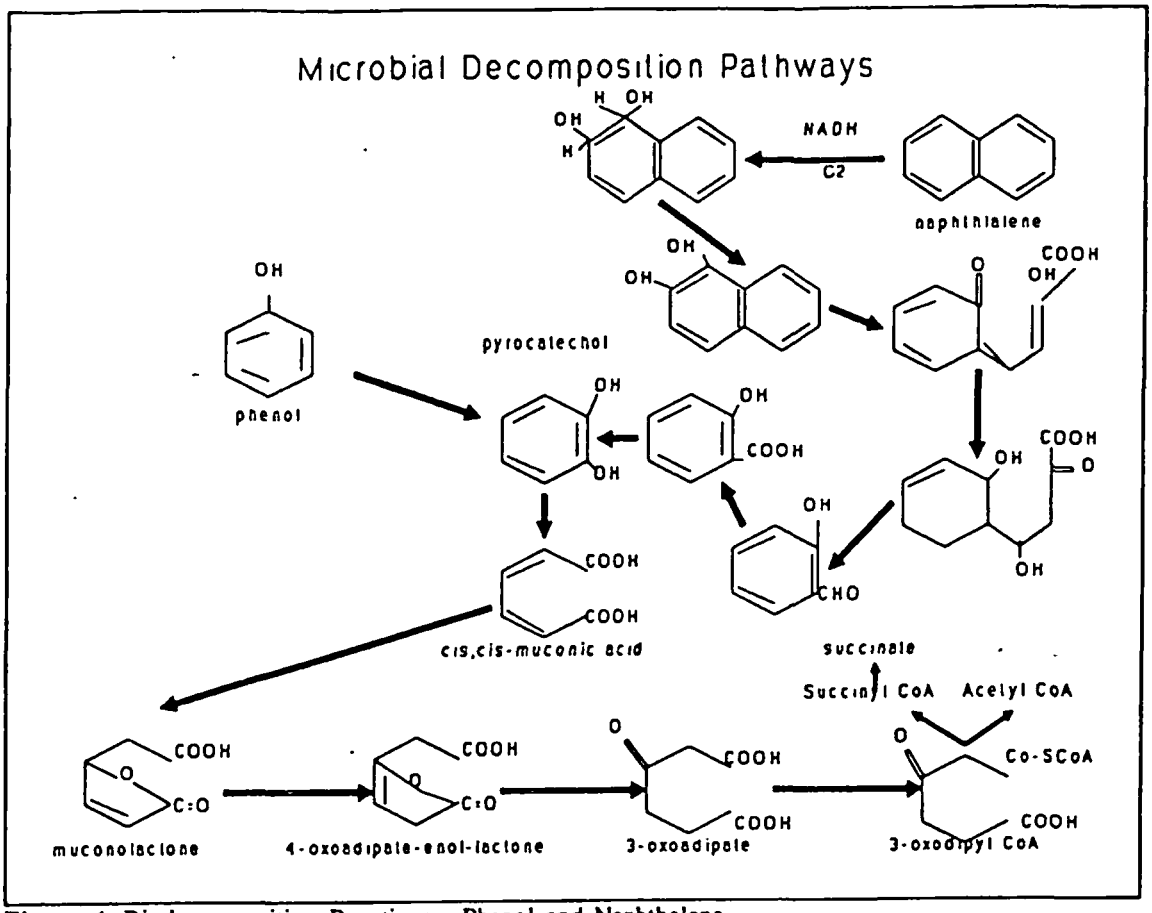

Figure 4. Biodecomposition Reactions - Phenol and Naphthalene

Conclusions

Biotreatment processes are technically viable treatment technologies for many types of industrial waste. Major advances in biotechnology and bioengineering research have improved biotreatment processes from a geological time treatment scale to acceptable reaction rates for industrial wastes. Many biotreatment processes are commercially available today and more methods will rapidly develop as the demand for waste clean-up increases.

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Report G-102a

Biotreatment of Cyanide Industrial Waste

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PINTAIL Systems, Inc.
Technical Report Series
Report No. G-102a

Biotreatment of Cyanide Industrial Wastes

Introduction

Cyanide is an industrial chemical that is used or produced as a by-product in mining, electroplating, aluminum and steel production, petroleum manufacturing and pesticide formulation processes. As such, cyanide is a high profile chemical that receives attention in regulatory, public, and industrial arenas. Potential environmental release into public waterways, groundwater or soils is a concern due to the reactivity and high toxicity of cyanide or easily dissociable cyanide compounds (Towill, et al). Trends in environmental regulation are progressively more conservative, requiring treatment of cyanide-containing wastes. This makes the waste mitigation an economic, as well as, environmentally important issue.

Although there are many physical and chemical mechanisms for cyanide treatment, natural biological methods for cyanide decomposition have lately received much attention. Biological treatment technologies for cyanide wastes have the advantage of being cost effective, efficient and do not replace one priority pollutant with another. This review explores the use of biological cyanide biodecomposition processes and presents a development flowchart for bioprocessing technology.

Pintail Systems, Inc. has experience in the development and design of bioremediation treatment systems for many problem wastes including cyanide and heavy metals from gold mining and aluminum manufacturing operations. Examples of bench-scale and pilot field tests are presented in the final portion of this review.

Biotreatment Technologies - Definition and Development

Biological treatment using natural bacteria is a familiar option for handling municipal and agricultural wastes (Metcalf and Eddy, Inc.). Bacteria can degrade many organic contaminants to harmless by-products through normal cellular metabolic reactions. The complexity, concentration and potential high toxicity of industrial wastes, however, often precludes the use of natural treatment systems. The key to industrial waste biotreatment is the discovery and adaptation of bacteria that are tolerant to toxic industrial wastes. Recent advances in bio-engineering and biotreatment technology indicate that an augmentation or natural enhancement of inherent microbial processes will produce industrial-scale remedies for cyanide biodecomposition.

Primitive bacteria are able to metabolize cyanide compounds because the first life forms developed in an environment that contained cyanide in both the atmosphere and oceans (Miller and Orgel). Cyanide serves as either a source of nitrogen or carbon for necessary cell building reactions in many of the simplest bacteria (Knowles). Radiolabeled tracer studies have proven that cyanide provides carbon or nitrogen for the formation of purines, pyrimidines, amino acids and many other organic intermediates (Oro and Lazcano-Araujo). Identification of cyanide-tolerant and cyanide-metabolizing bacteria is one of the first steps in making an industrial biotreatment process.

Although bacteria with these cyanide degradation potentials do exist, they usually are found in a complex microbial ecosystem. Other types of bacteria that cannot use cyanide usually predominate and competitively inhibit the formation of a dominantly cyanide decomposing population. The next step in creation of an industrially useful biotreatment method is, therefore, the bioaugmentation of the native bacteria that use cyanides.

Bioaugmentation is defined as the addition of selected bacteria to a biological treatment process to enhance a desired reaction (Kobayashi). Aug-

mentation improves bacteria through conventional selective culturing techniques and capitalizes on naturally occurring random mutations to amplify desired characteristics in the population. The bioaugmentation procedures are also meant to inhibit or eliminate any competing bacteria that do not participate in the treatment processes. The result of a successful bioaugmentation is a population of natural bacteria that is fine-tuned for the target waste treatment.

The next step in the biotreatment development is the adaptation of the treatment bacteria to the waste. Other components of the waste stream such as heavy metals, fluorides, chlorides or complex organics can be toxic to the treatment bacteria. A biotreatment population must be tolerant of all potential waste components or be able to remove other targeted toxins from the waste stream.

Finally, industrial biotreatment development involves the manufacture, concentration, preservation and pilot testing of the augmented and adapted treatment bacteria. A constant, reliable source of the bacteria must be available for continuous treatment systems. A specially adapted population is subject to losing its waste biotreatment abilities through mutation or environmental upset. A long-term remedial bio-action must, therefore, allow for continuous replacement of the working bacteria with fresh working strains.

A complete biotreatment development program is summarized in the flowchart detailed in Figure 1. Formation of biological methods for industrial cyanide wastes is a complex but feasible treatment technology. The final section of this review summarizes existing cyanide waste biotreatment processes developed by PSI's research and environmental engineering staff. Examples of cyanide biotreatment for gold mining and aluminum manufacturing wastes are presented. Other cyanide pollutants amenable to biotreatment include aqueous and solid wastes from electroplating, steel manufacturing, coke production, pesticide formulation and petroleum manufacture.

Existing and Potential Cyanide Biotreatment Technologies

Cyanide wastes generated from gold mining and processing, pesticide manufacture, aluminum manufacturing and electroplating operations are wastes that can be treated by existing biological treatment technology. The two biotreatment methods that have been demonstrated in industrial-scale operations are: 1) enzyme treatment systems and, 2) bacterial cyanide decomposition processes. An enzyme treatment system is most applicable to higher concentrations of free cyanide in aqueous solution and the bacteria methodology is best for remediation of lower concentration total complexed metal-cyanides in aqueous and solid waste. Both systems are commercially available and have been used in large-scale treatment schemes.

Enzyme Treatment System

A direct enzyme treatment system uses the enzymes isolated from bacteria for contained, batch treatment systems. Enzyme systems mediate the oxidation of cyanide which forms carbon dioxide and ammonia as by-products. Enzymes such as cyanide hydratase, rhodanese and various nitrilases have been isolated and identified as active in cyanide metabolism by bacteria (Westley). The purified enzyme contacts the aqueous waste in a batch process. This treatment method is best used at high levels of free cyanide (2000-10,000 mg/L) and is not economical for low levels of cyanide or metal-cyanide complexes. An example of this process is the 'Cyclear' preparation by ICI (Clarke).

A sample process is diagrammed in Figure 2 and typical cyanide decomposition for enzyme treatment is shown in Figure 3. Advances in biotechnology have shown how enzymes can be isolated, identified and mass produced for industrial applications. Pintail Systems R & D staff is actively researching the isolation and mass production of a variety of cyanide decomposition enzyme systems.

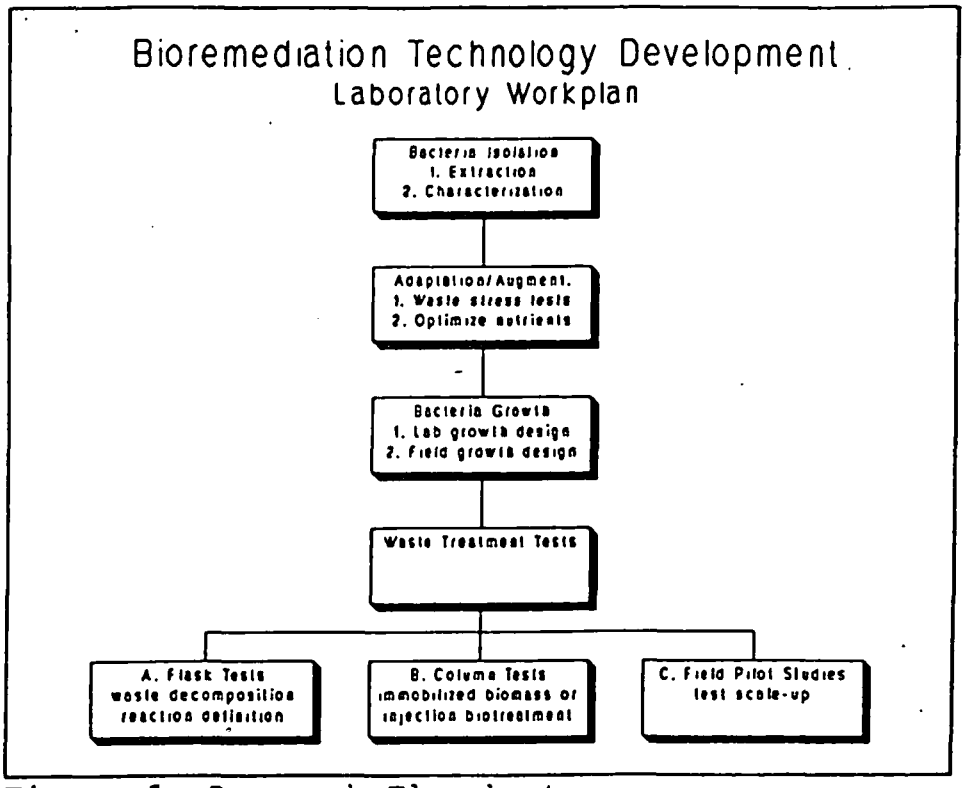

Figure 1. Research Flowchart

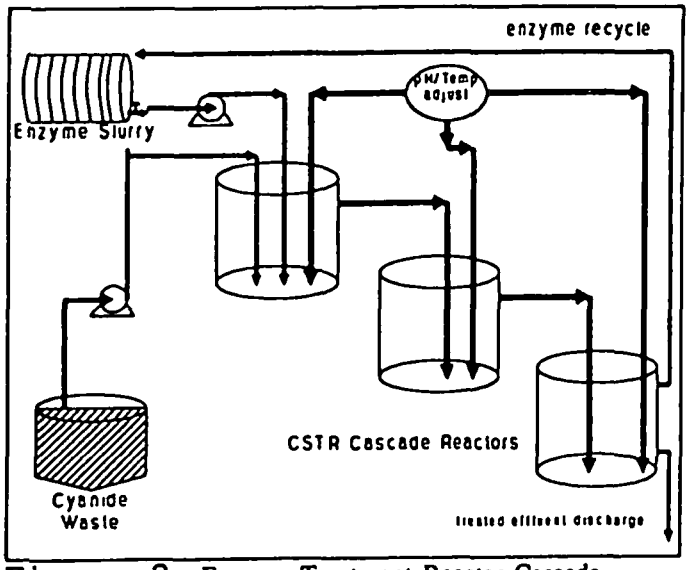

Figure 2. Enzyme Treatment Reactor Cascade

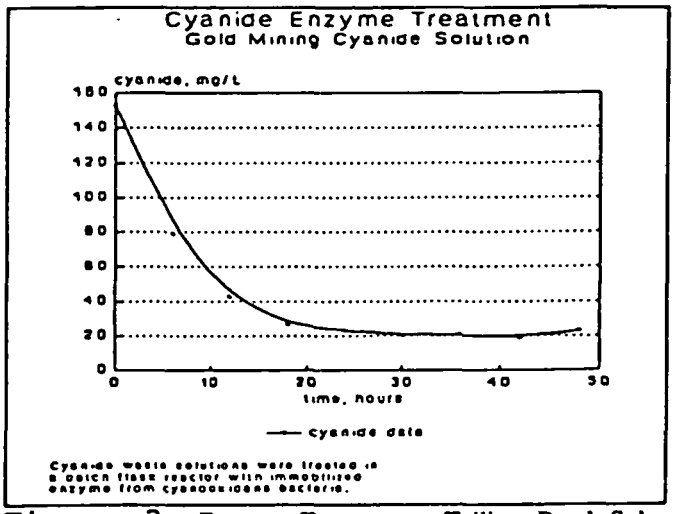

Figure 3. Enzyme Treatment - Tailing Pond Solution

Biological Treatment System - Cyanide-Contaminated Mining Wastes

A biological treatment of cyanide-containing waste can be designed to treat aqueous effluents in suspended or attached growth plants. It is also possible to treat soils or solids in *in situ* treatment with bacteria solutions. Cyanide waste from gold recovery and cyanide produced in aluminum manufacturing are two sources that are amenable to biotreatment. Gold mining operations in the U.S.A. (Mudder and Whitlock) and Soviet Union (Ilyaletdinov, et al) have used bacterial treatment systems for aqueous cyanide effluent treatment. Bacteria on rotating biological contacters remove thiocyanates and weakly complexed metal cyanides from discharge and process water. The treatment is efficient and effluent meets regulatory discharge standards. This type of treatment effects a >98% removal of thiocyanates and weak acid dissociable cyanide.

Pintail Systems staff has demonstrated successful treatment of solid residue from gold recovery operations and aluminum manufacturing. Each waste presents special problems for bioremediation. Wastes from gold mining include process water, cyanide leached ore residue and tailings. *In situ* mitigation schemes were designed using biologically augmented treatment bacteria and scale-up culturing and contact methods. A series of bench-scale flask tests, pilot plant column tests and field demonstration programs confirmed that biotreatment systems were effective with both aqueous and solid waste treatment.

To develop the *in situ* biotreatment for solid ore residue bacteria were isolated and augmented. Microbial assays of cyanide-leached mining residue showed that native bacteria were established in the residue when total cyanide concentrations were below 30 mg/kg TCN. The bacteria found in older residue and mine district samples were identified as mixed populations of both spore-forming and non-spore forming bacteria. After cyanide stress and subculture in a chemically defined medium, a population was found that had significant cyanide degradation potential. A comparison between native bacteria and biologically augmented populations for cyanide decomposition is shown in Figure 4.

To test the microbial cyanide decomposition, a series of bottle tests, column tests, a 1500 ton and a 20,000 ton field test were designed. The bottle tests were planned using 500 grams of minus 10 mesh ore residue and column studies used 100 kg of minus 3/4 inch residue packed in 6" x 10' PVC columns. A 1500 ton field test used minus 3/4 inch residue stacked 16 feet high on an impermeable liner. The 20,000 ton field test was run in a controlled area of a residue dump. Test areas were marked off to study effects of natural weathering, water washing, bacteria washing and direct bacteria injection. Results are presented in Table I for bench-scale testing and Table II for the column tests. Figures 5 and 6 compare cyanide decomposition between control and biotreatments in the field pilot tests.

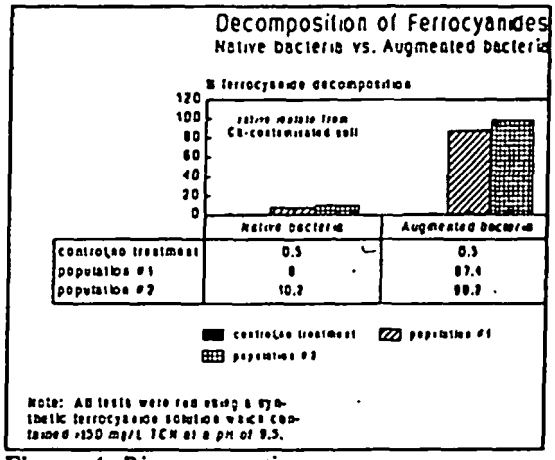

Figure 4. Bioaugmentation

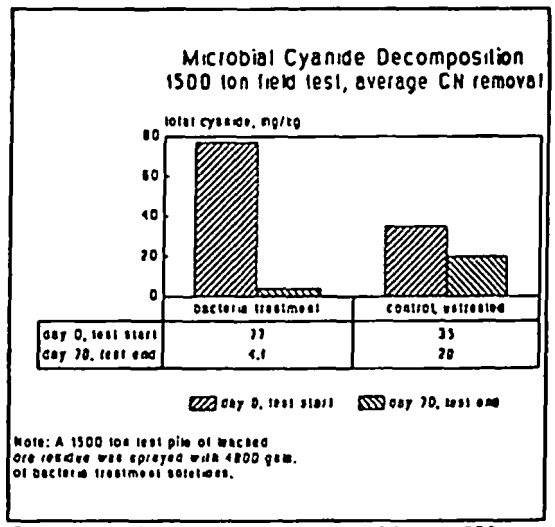

Figure 5. Cyanide Biodecomposition, 1500 ton field test.

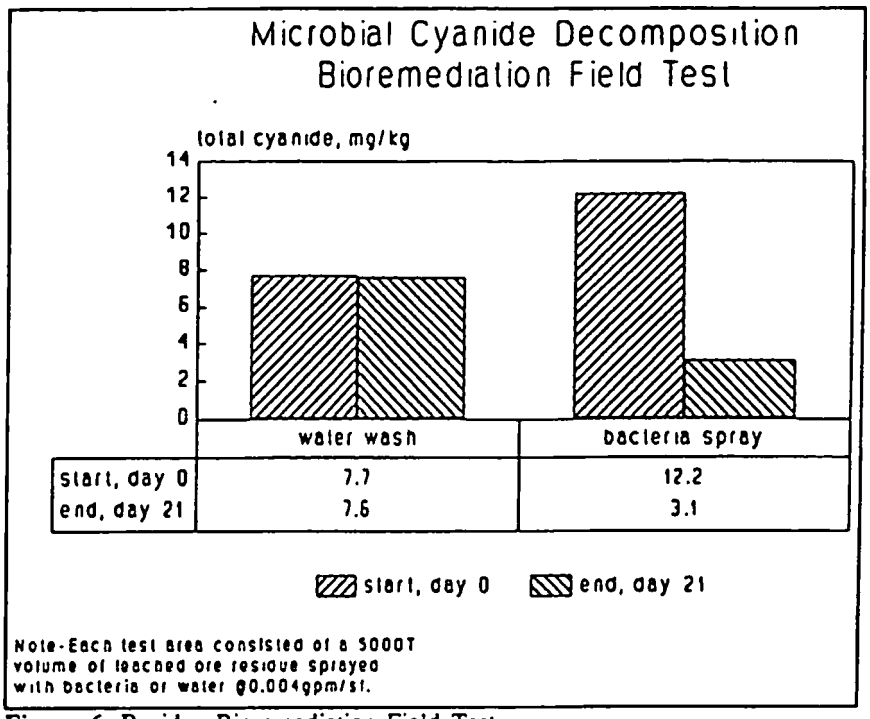

Figure 6. Residue Bioremediation Field Test

Table I. Bench-scale Cyanide Biodecomposition

	Flask Cyanide Decomposition			
Flask ID	total CN, mg/kg test start 0 hours	total CN, mg/kg test end 48 hours	% CN removed chem/physical decomposition	% CN removed biodecomposition
#1, OR-4 bacteria	123.	<0.1	50-60	40-50
#2, " "	135.	0.9	50-60	40-50
#3, " "	130.	0.4	50-60	40-50
control, Sterile H_2O	117.	53.0	54.7	<1

Experiment Design: 500g of a -10 mesh leached ore residue were inoculated with 20 mL of treatment bacteria solution or sterile deionized water. Flasks were incubated at 21°C for 48 hours. Total cyanide in leached ore residue was determined by extraction in 5% NaOH and a reflux acid distillation. Residue pH = 8.9, treatment solution or water pH adjusted to 9.0

Note: Chemical and physical decomposition remove free and easily dissociable metal cyanides.

Table II. Column Tests - Cyanide Biodccomposition

Column Tests - Cyanide Biodecomposition

Column ID	total CN mg/kg start, Day 0	total CN mg/kg end, day 21	% decomp
#1, OR-2 bacteria	125	<0.1	99.9
#2, " "	119	0.5	99.6
#3, " "	130	<0.1	99.9
#4, " "	108	0.2	99.8
#5, control (H_2O wash)	127	49.3	61.2
#6, control "	131	57.0	56.5

For each test 100 kg of a fresh leached ore residue were loaded into a 6"x10" vertical PVC column. One pore volume of bacteria solution or sterile deionized water were applied in a percolation leach. Ore residue was tested for total cyanide by extracting with 5% NaOH and distillation of extracts in a reflux acid distillation.

Biological Treatment - Aluminum Manufacturing Cyanide Wastes

Pintail Systems has completed two phases of research and development for biotreatment of cyanide waste from aluminum manufacturing. Cyanide is a primary contaminant of spent potliner and cathode material from aluminum manufacturing processes. Most of the cyanide exists as an iron cyanide and ranges up to 0.5% concentrations. Biotreatment is complicated by the extreme pH (>11.5) of spent potliner and leachate solutions and by high concentrations of fluoride.

Biological treatment processes were developed by the classical bacteria isolation/augmentation/testing sequence. The bacteria for these waste treatment tests consist of native isolates and of strains previously tested in high pH solid waste that contained both ferrocyanides and soluble fluorides. Two strains will be used in the waste biotreatment flask tests - the existing strains adapted to both spent potliners and extracted native bacteria grown to working concentrations.

Adaptation and augmentation of existing bacteria was accomplished by contacting a log phase growth population with the waste source in an aqueous, dilute medium. The dilute media was intended to act as a secondary stress and force the surviving bacteria to rely on the waste as a nutrient source. Growth in the adaptation flasks in the presence of the waste was monitored for a period of two weeks to plot log phase, stationary and death phases of the adapting population.

Both the augmented native populations and the adapted stock bacteria were tested for ability to decompose total cyanide in a synthetic ferrocyanide solution and in an extract of spent potliner material. These experiments were designed to confirm the suitability of the treatment bacteria for the flask studies.

An initial treatment of the aged spent potliner was run in a percolation leach plan for both the treatment solutions and a water wash control. The columns were set up as shown in Figure 5. The percolation leach was chosen as the closest model to an *in Situ* treatment program. In the percolation leach a biotreatment solution or a water wash control solution is trickled over the spent potliner (as-received particle size) contained in a 2" x 48" PVC column. Leachate solutions from both columns were collected daily and analyzed for total cyanide.

Test results for flask and column spent potliner treatments are shown in Figures 6 and 7. The bacteria adapted for this waste treatment proved to work well at pH >12 and high fluoride concentrations.

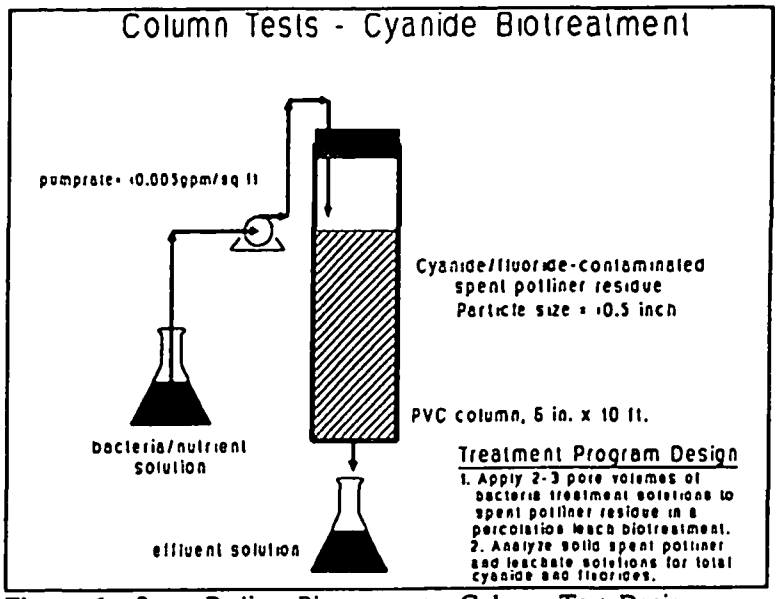

Figure 6. Spent Potliner Biotreatment - Column Test Design

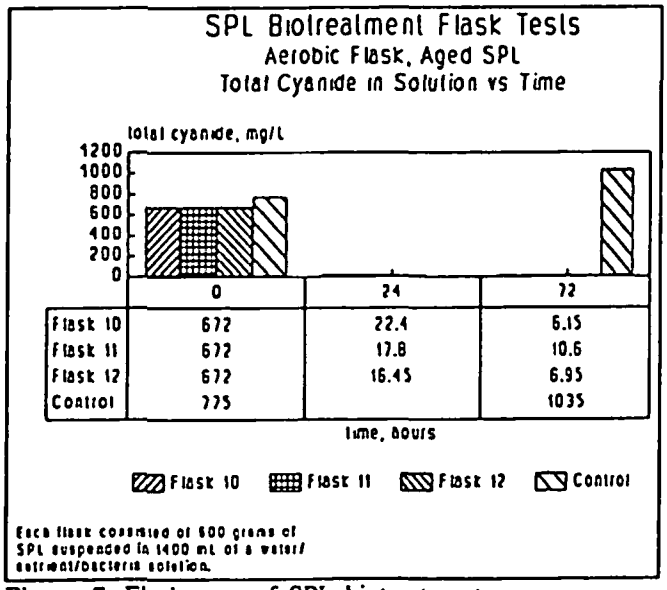

Figure 7. Flask tests of SPL biotreatment

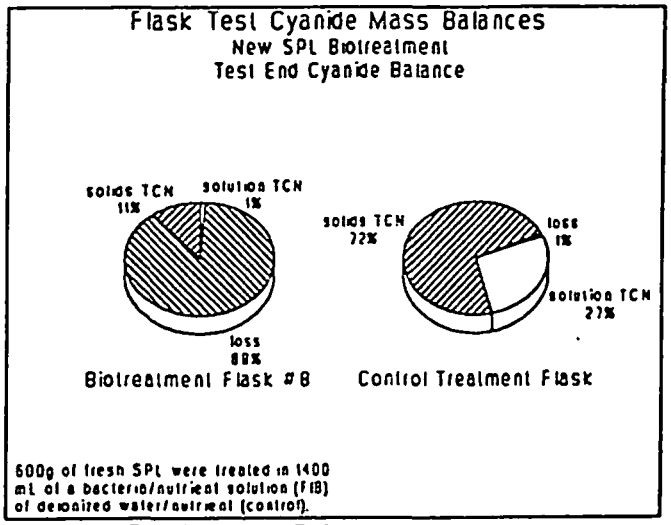

Figure 8. Cyanide Mass Balance

Conclusions

These bioreatment methods present economic solutions for cyanide-contaminated solid wastes from the mining and metal finishing industries. They also present an alternative to some of the costly, inefficient and environmentally hazardous alternatives of containment or chemical treatment. Although natural methods of cyanide decomposition are adequate for many environments, a biotreatment is a desirable option where traditional treatments are costly or only partially effective.

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Report G-114

Bacterial Treatments for Metal Accumulation and Re-Mineralization

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PINTAIL Systems, Inc. Report N. G-114
Environmental Technical Report Series

Bacteria Treatments for Metal Accumulation & Re-mineralization

Introduction

Heavy metals form a significant portion of the pollutants found in our toxic waste dumps and are increasingly present in industrial wastewaters and natural surface and groundwater. Biological treatment methods for metal-laden waste streams are receiving attention as a natural process alternative to traditional removal methods (Ebner). Many different processes using living (Townsley) and non-living microorganisms (Brierley) for metal accumulation have been developed in recent years.

Metal waste from electroplating, mining and metal processing industries have traditionally been treated by chemical and physical processes (Cushnie). These include hydroxide precipitation, chemical oxidation or reduction, evaporation, ion exchange, ultrafiltration, electrolysis and electrocoagulation. Many of these processes are costly and are not a complete solution to the problem of environmentally acceptable metal disposal. Recycling efforts, including bacterial metal accumulation, are receiving renewed attention because of the high costs and long-term liabilities associated with traditional treatment methods. Innovative recycling of metal wastes promises economic and environmental benefits for both industry and regulatory agencies. Pintail Systems, Inc. has developed several microbial treatment processes for a variety of heavy metal waste types.

Microbial sequestering of metals is a treatment technology that is applicable to waste streams from mining operations, electroplating and metal finishing processes. Heavy metals that impact groundwater quality from abandoned and operating mining districts are also potential targets for innovative natural technologies. In addition to the advantages of low cost and the possibility for *in Situ* treatment, microbial processes can be engineered to be specific for a unique waste. The specificity of biological processes eliminates the requirement for pre-treatment and complex treatment facilities.

Technology Description

Numerous species of bacteria, fungi and yeasts are capable of accumulating many times their weight in heavy metals (Eccles and Hunt). Both living and dead biomass are effective in removing soluble metals from waste streams containing metals such as gold, silver, chromium, cadmium, copper, lead, zinc, cobalt and others (Zajic). These metals can also be immobilized in soils by bio-mineralization reactions for in place treatments. There are two basic mechanisms involved in metal uptake by bacteria:

1. Accumulation by surface binding to the bacterial cell wall or extracellular materials.

2. Uptake into the cell for use in metabolic processes as necessary nutrients.

Surface binding is capable of accumulating the largest amount of metals from solution. Intracellular uptake of metals to meet nutritional needs is typically responsible for a minor contribution to overall metal removal (Fenchel and Blackburn). The surface binding mechanisms include:

* complexation of metals with organic compounds;
* precipitation caused by ion exchange or production of oxalic acid in the cell;
* chelation by cell membrane components such as pigments, phenolic polymers, cellulosic ligands or chitin.
* remineralization of metal species as a result of complex interaction with extracellular by-products of bacterial metabolism.

Biomineralization cycles are accepted as part of the natural cycling of minerals and metals in the global environment (Westbroek and DeJong). The keys to development of commercial biotreatment systems are choice of the best bacteria and creation of conditions that will simulate and accelerate natural processes. The diversity of biochemical

reactions for metal removal or re-mineralization shows that treatment systems can be individually engineered for many waste types. Various populations of bacteria can also be selectively enhanced to remove target metals from a waste stream. The selectivity leaves non-toxic metals in solution, thus extending the life of the treatment system.

The steps necessary to the development of an effective biotreatment system for metal removal from aqueous waste streams are summarized in Figure 1. A number of bacterial processes have been researched and tested for metal removal. Commercial processes are available from Pintail Systems using fungal biomass, live immobilized biomass, dead biomass, and suspended growth natural treatment systems. Each process is ideal for certain waste types and treatment designs. Some of the limitations include waste specificity, volume restrictions and treatment system maintenance. Other restrictions for *in situ* biotreatment consist of climate control problems, nutrient limitations and presence of other toxic components. These liabilities can all be mitigated by engineered solutions to each technical problem.

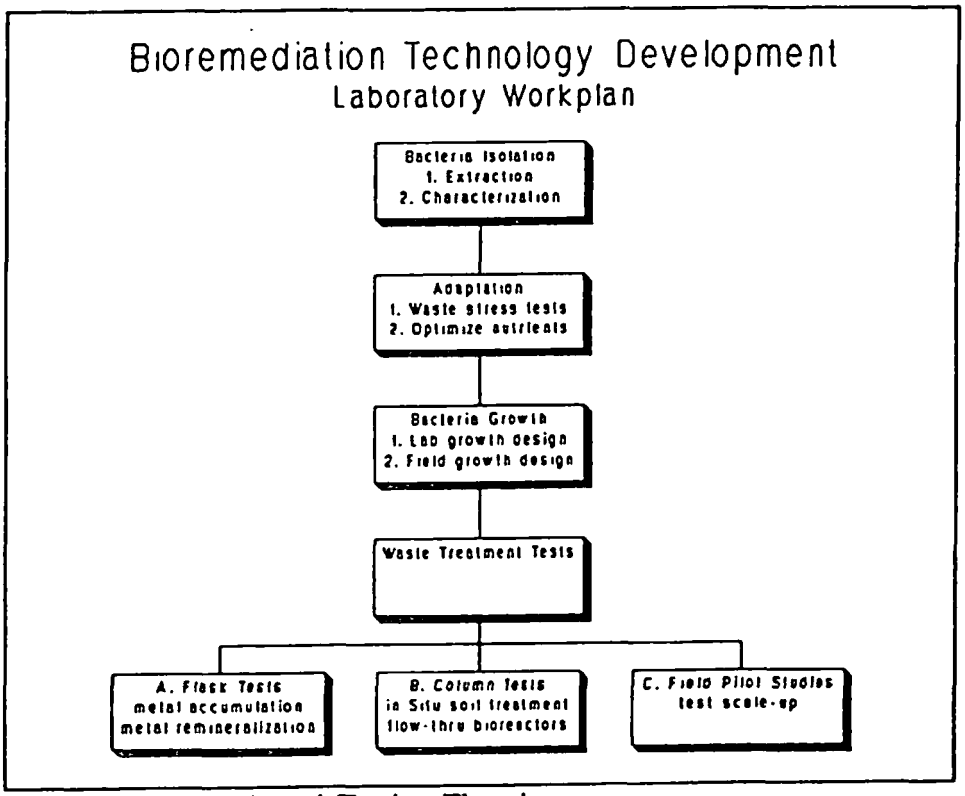

Figure 1. Research and Testing Flowchart

Suspended growth, attached growth, and fluidized bed treatments have been tested for metal accumulation by Pintail Systems in research and commercial applications. A treatment system that works for metal extraction for electroplating sludges or wastewaters is not necessarily the best system for removing metals from acid mine drainage wastewaters. The solution to natural treatment development is adapting the bacteria for the specific waste type. Bench-scale test work for each biotreatment system includes isolation and augmentation of working bacteria followed by tests with synthetic and real wastes to maximize the treatment.

Some of the waste types appropriate for bacterial treatment processes include:

1. Electroplating wastewater: Fluidized bed extraction of metals by live biomass immobilized on inert support matrices.

2. Electroplating sludges: Biological extraction of metals and metal-hydroxide precipitates in bioreactor systems followed by concentration and recovery of metals.

3. Acid mine drainage: Biological pre-treatment in biological fluidized bed extraction followed by a secondary polishing procedure in a wetlands treatment system.

4. Metal refining wastes: selective removal of target metals in aqueous treatment systems or metal immobilization in soil and solids. The selective sequestering also may have applications for metal finishing processes.

5. In situ metal immobilization: metal contaminants in soil or solid waste are immobilized and rendered environmentally inert by biomineralization reactions.

A final advantage of natural biological treatment technology is that the end products are natural and non-toxic (Ehrlich). Removing metals from a waste stream by natural methods can constitute an end to responsibility for the waste. Re-mineralization of mobile metals also promises to be a cost effective treatment for contaminated soils and waste solids.

Pintail Research Program Summary

Development of successful bioremediation technology for heavy metal wastes has involved innovative microbial research design. The goals for any treatment system include the basic steps of adaptation/augmentation/testing. These steps defined below, are the solution to biotreatment development for unique waste streams.

* Adaptation: Proven biotreatment bacteria or indigenous bacteria are added to a waste source to allow the population to acquire a high tolerance to the waste.

* Augmentation: The adapted bacteria populations are grown to working strength in several chemically defined nutrient broths. Selective enhancement of the population eliminates the non-working components and insures time and cost effective bioremediation populations.

* Test Work: Bench-scale and pilot-scale tests are designed to confirm the biotreatment potential of each population for a specific waste source. Test data is used as proof of the feasibility of biotreatment and is also incorporated into the engineering design for field pilot tests.

An example of the process of adapting and augmenting a treatment population is shown in Figure 2. In this case, a population of bacteria was isolated from a dominantly inorganic, metal-laden environment. The native bacteria showed a slight ability for natural removal of copper, lead, zinc, nickel or cobalt. After adaptation and augmentation to a specific waste source, the bioaugmented treatment bacteria showed an improved capacity for metal removal from aqueous waste streams. The theoretical metal removal efficiency was demonstrated using synthetic metal solutions containing at least 150 mg/L of heavy metals.

Bioaugmented bacteria have also been successfully enhanced to show specific removal of only target metals from solution and to leave non-toxic metals in solution. This aspect of biotreatment has application with waste streams that contain mixed metals in solution. Some of the metals may be toxic and others may pose no threat to the environment. In these cases, a conventional treatment system can become overloaded by large quantities of the non-toxic metal removal. The bioaugmented bacteria have the ability to extend the life of the treatment system through specific metal accumulation. This treatment is demonstrated in Figure 3. A biotreatment population was adapted to a waste source that contained less than 1000 mg/L each of copper, nickel and zinc. The waste also contained more than 10,000 mg/L of iron which threatened to overload the biological treatment capacity. The population was changed to be specific for copper, nickel and zinc and proved to pass iron in solution through the treatment media.

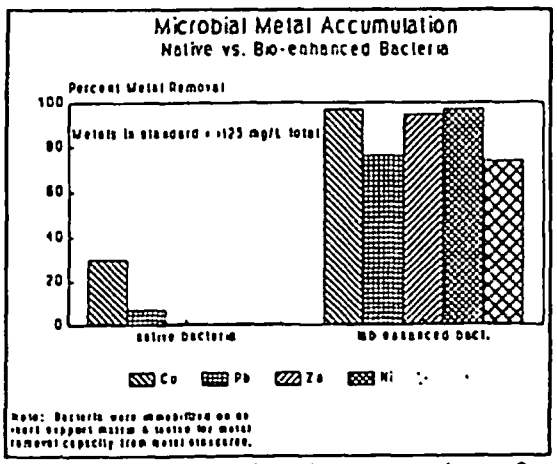

Figure 2. Bacteria Augmentation for Metal Accumulation

A final criteria investigated by Pintail Systems for treatment design is the actual capacity of the technology for metal removal. The data from these metal loading tests is critical to system design and cost analysis for final treatment plants. Biotreatment systems have to compete with conventional treatment technologies in a variety of environments and cannot be cost effective if they are material or labor intensive. For this reason, a series of metal loading tests have been conducted with both synthetic and actual waste solutions. An example of the treatment system life is shown in Figure 4.

Ongoing research is targeting industrial applications for biotreatment in metal finishing and recovery operations. Bacteria could be used in precious metal recovery circuits as well as base metal waste recycling. Many microbial treatment systems have the advantage of inexpensive regeneration of treatment bacteria from inert biomass. New treatment bacteria can also be grown economically for live biomass treatment applications. The versatility of microbial metal sequestering promises many new research applications for these natural technologies.

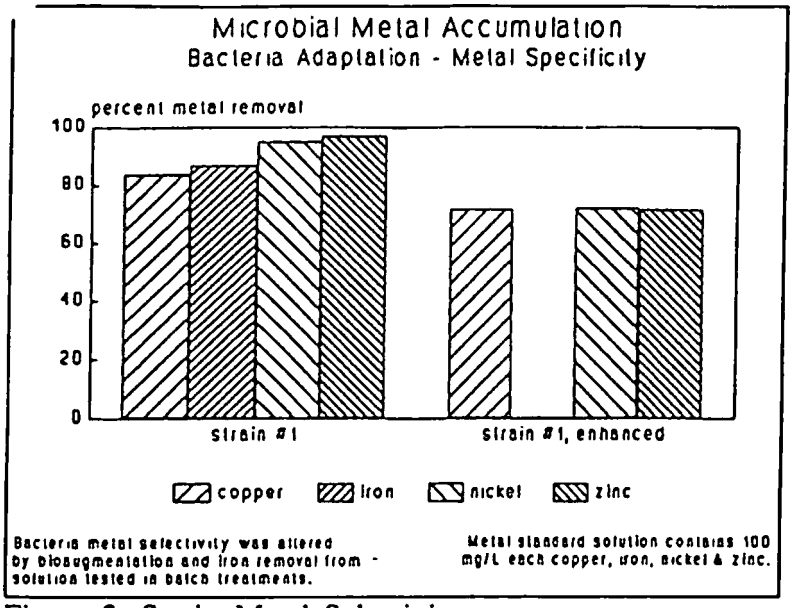

Figure 3. Strain Metal Selectivity

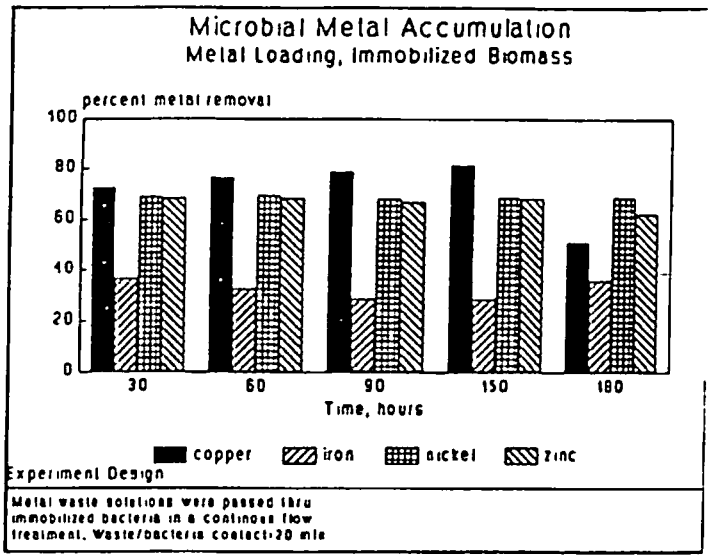

Figure 4.Continuous-flow Biotreatment

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MICROBIAL DEGRADATION OF METAL-CYANIDE COMPOUNDS IN SOLID MINING WASTE

L.C. THOMPSON

Cyanide has been used in the commercial recovery of gold and silver for nearly 100 years and is currently used in the closed-circuit heap leaching process. After leaching, the ore residue is water-washed to recover most of the cyanide. Metal-cyanide complexes are left though, as a trace contaminant in the solid residue.

Current trends in environmental regulation are pointing towards complete treatment for all types of waste. Potential regulation of treatment that is now voluntary means that degradation of cyanide wastes has become economically, as well as environmentally important to the gold mining industry. Solid ore residue that has been leached of gold and silver in a cyanide process may be regarded to be a point source of cyanide pollution unless the residue is completely encapsulated or treated. High costs of complete containment or chemical treatment have made microbial degradation more attractive. Biological treatment technology is available for cyanidation waste waters but to date, there has been no economical biological treatment for solid waste material.

This research basically had two goals:

1. To isolate any strains of bacteria native to the solid residue that could tolerate and potentially use complexes metal-cyanides to meet nutritional needs.

2. To isolate and stress the bacteria strains to obtain a population that would enhance the natural degradation of cyanide compounds.

The natural degradation of complexed cyanide is likely to be a combination of oxidation, photo-decomposition and microbial degradation. The more stable metal-cyanide complexes such as the ferro, gold or cobalt cyanides are not naturally decomposed in a solid waste matrix. Natural biodegradation of these complexes is not likely, due to the potential toxicity of both the cyanide and the heavy metals to the bacteria. It was therefore necessary to find strains of bacteria that could tolerate both cyanide and heavy metals, use cyanide as a carbon and/or nitrogen source and accumulate metals.

Microbial assays of cyanide-leached mining residue were conducted to determine presence of bacteria at different levels of total cyanide in the residue. Freshly leached and water-washed residue typically has 100-150 mg total cyanide per kilogram of residue. Bacteria were found to be established only when total cyanide values had dropped to less than 30 mg/kg total cyanide through natural attenuation and removal mechanisms. The bacteria

found in this older residue were identified as a mixed population of both spore-forming and non-spore forming bacteria. Bacilli, Thiobacilli and Actinomyces were specifically identified as showing promise for cyanide biodegradation and metal tolerance.

Samples of all three types of bacteria were cultured in enrichment media with up to 100 mg/L cyanide (as a sodium cyanide). A culture provisionally identified as a mixed Bacillus population showed some promise in both cyanide tolerance and degradation after serial subculture in a Bacillus isolation/sodium cyanide broth. This culture, however, was not as active in bench-scale tests with leached ore residue.

A mixed population of native bacteria was isolated from a sulfide ore residue and subcultured for cyanide tolerance and degradation. After cyanide stress and subculture in a medium designed to approximate residue dump conditions, a population was found that had significant cyanide degradation potential.

To test the microbial cyanide decomposition, a series of bottle tests, column tests and a 1500 ton field test were designed. The bottle test used a 1 kg sample of minus 10 mesh residue. Column studies were run with 250 kg of minus 3/4 inch residue packed in 6" x 10' plexiglass columns. The 1500 ton field test used minus 3/4 inch residue stacked 16 feet high on an impermeable liner. Results are presented in Table I for test samples and controls.

Table I. Biotreatment of Solid Leached Ore Residue for Cyanide Decomposition

	Residue Total Cyanide (mg/kg)		
test id:	Bottle Test	Column Test	Field Test
time:	72 hours	14 day	21 day
start/end values:	start/end	start/end	start/end
Biotreatment	123. <0.1	125. <0.1	77.0 3.8
Control (water-wash)	117. 53.0	127. 49.3	27.0 23.1

Note: In wash wash control tests, soluble metal-cyanide compounds are relocated through dilution and physical transport but are not decomposed.

Historical data collected from a 5 million ton residue pile indicates that natural decomposition takes total cyanide values to less than 30 mg/kg total cyanide in less than 6 months. Total cyanide values then remain at 10-30 me/kg for at least five years. An enhanced microbial cyanide decomposition scheme clearly shows many advantages for detoxifying solid waste residue.

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BIO-LEACHING OF SULFIDE ORES

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Depletion of known ore reserves and increased demand for precious metals have caused a revolution in biohydrometallurgical processing technology for gold recovery. Known ore deposits and future discoveries are most likely to be lower grade sulfide ores that can be difficult to recover with current leaching technology. Future metal recovery operations will increasingly use bio-oxidation techniques.

Bacteria are an integral part of mineral cycling and mineral transformation in nature. Although biological processes are recognized as part of the mineralization and oxidation reactions in some ore deposits, they have only recently been applied to enhancing metal recovery in hydrometallurgical procedures. This paper explores the traditional metallurgical application of biological leaching and oxidation reactions and reviews the complete range of bacteria available for metal recovery systems. Pre- treatment of ores with bacteria improves metal recoveries in tank leaching systems and shows promise for heap leaching methods.

Introduction

There is no longer any question that bacteria play a natural role in the on-going transformation of some ore deposits (1,2). As applied to sulfide ores, a few strains have been specifically identified that exhibit a natural leaching potential (3). These bacteria can be isolated from waters and soils in old mining districts where they contribute to continuing leaching and pollution problems in acid drainage and heavy metal solubilization. Sulfur and iron bacteria as well as many heterotrophic strains have also been found in ore deposits and sedimentary rocks at depths up to 2000 meters (4). Their presence in both ore deposits and processed ores shows the microbial association with natural leaching and the potential role that bacteria can play in the development of new leaching technology.

The bacteria that are most likely to be found in these specialized environments are the chemolithotrophs, or those bacteria that derive all of their nutrient requirements from inorganic sources. Bacteria included in this category are the genera Thiobacillus, Thiomicrospira, Sulfolobus, Desulfovibrio and Beggiatoa. The cells use iron and sulfur as sources of nutrients for growth, bio-energetics and replication. Any bacteria population mix in these specific environments is in a state of flux where succession populations develop as the environment or the character of the deposit changes. There is evidence that Thiobacillus ferrooxidans is one such bacteria that becomes dominant under aerobic conditions and performs the final stages of sulfide ore transition (5). Other native bacteria operating in a wide range of optimal temperatures, pH, pressure and nutrient media also have the potential for development as bioleaching populations.

Bio-leaching or bio-oxidation processes are essentially metal accumulation/ biomineralization cycles that could be developed as a bioengineered solution for increased precious metal recovery from sulfide ores. The key to the process development is understanding the natural role bacteria can play in ore deposit formation and transformation. Natural processes take place on a geologic time scale and the answer to engineering both time and recovery improvements is found in new bioaugmentation techniques. Bioaugmentation can be best described as the use of microorganisms that have been selected for desirable natural traits and that have then been enhanced in the laboratory. Augmenting a population selectively eliminates competing, non-working bacteria and amplifies the desired characteristics of the working microorganisms. These methods take natural reactions one step further and create a specialized leaching population through selective culturing and randomly induced mutations. The remainder of this review identifies the selection, adaptation and augmentation techniques currently being used or developed in biohydrometallurgy research.

Identification of Ore Transformation Bacteria

Sulfur cycles and oxidation/reduction of metals are the most important reactions to consider in development of bioleaching technology. The wide variety of bacteria that participate in these reactions in nature implies that evolution of specialized bio-oxidation populations should be theoretically possible for most ore-specific leaching problems. It is important to look at both sulfur and iron cycles, as the by-products of one can be either inhibitory or necessary to the other.

The Thiobacilli are unique because they are able to derive all of their energy requirements from the oxidation of inorganic sulfur. These reactions consist of both assimilatory and dissimilatory redox reactions involving sulfides, thiosulfates, elemental sulfur and tetrathionates. The temperature and pH conditions are also significant due to the formation of a variety of rate-limiting or insoluble by-products. The basic sulfur cycle detailed in Figure 1. shows the formation of reaction products and their place in the cycle. Both aerobic and anaerobic bacteria figure in different parts of the sequence. Many equilibrium reactions exist within these transformations and complimentary reactions provide a symmetrical system of synthesis and decomposition.

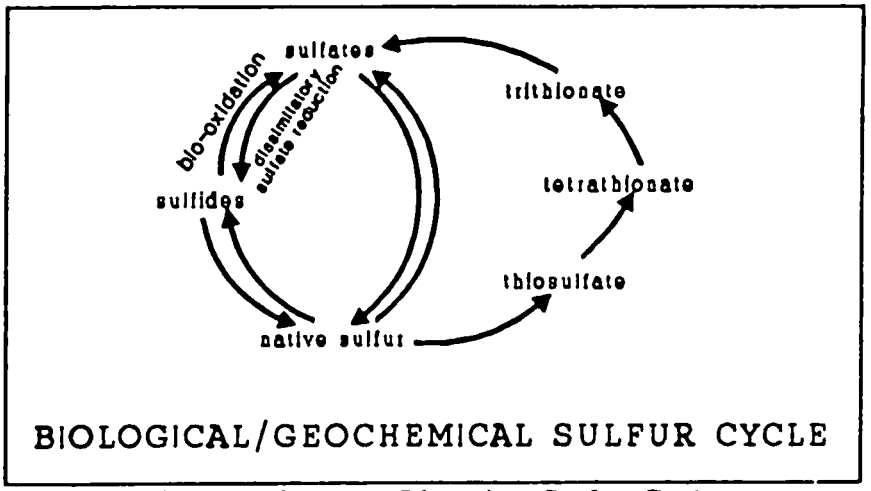

Figure 1. Geochemical and Biological Sulfur Cycles

The sulfur bacteria are defined as any chemotropic microbial population capable of oxidizing inorganic sulfur compounds for the generation of energy. Sulfur bacteria are included in the genera Achromatium, Macromonas, Thiobacterium, Thiospira, Thiovillium, Beggiatoa, Thiothrix, Thioploca, Thiobacillus and Thiomicrospira (6).

The bacterial oxidation of metal sulfides such as pyrite is a complex process which is dependent upon a number of environmental factors such as pH and the presence of oxygen. The most thoroughly studied microorganism regarding sulfide oxidation is Thiobacillus ferrooxidans which grows at an optimal pH range between 2.0 to 3.5 (7). Iron is necessary to many life processes in bacteria as a chelating agent, for nitrogen fixation in some microbes, and as a terminal electron acceptor for cell energy reactions. The processes are a combination of biologically catalyzed reactions and chemical reactions that can potentiate the oxidation of various metal sulfides. The dominant bacterial reactions involving iron are summarized in the following equations.

The oxidation of pyrite by T. ferrooxidans is a pH dependent reaction occurring below pH 4.0. Ferrous sulfate and sulfuric acid are the main reaction products, illustrated by

$$FeS_2 + 3.5\ O_2 + H_2O \qquad FeSO_4 + H_2SO_4 \qquad (1)$$

The system pH drops due to the acid formation and can alter the environment on a microenvironmental scale or, over time, on a macro-environmental scale. The ferrous sulfate that is formed is further oxidized by either Thiobacillus ferrooxidans or T. thiooxidans to form ferric hydroxide or ferric sulfate.

$$4\ FeSO_4 + O_2 + 2\ H_2SO_4 \qquad 2\ Fe_2(SO_4)_3 + 2H_2O \qquad (2)$$

At an elevated pH, the ferric iron will be hydrated to form an insoluble ferrous oxide.

$$Fe_2(SO_4)_3 + 6\ H_2O \qquad 2\ Fe(OH)_3 + 3\ H_2SO_4 \qquad (3)$$

The ferric ion is a strong chemical oxidizing agent which will chemically oxidize pyrite. The ferric ion remains in solution at a pH <3.0 and will continue to catalyze the reaction which yields more ferrous iron.

$$FeS_2 + Fe_2(SO_4)_3 \qquad 3\ FeSO_4 + S^\circ \qquad (4)$$

The dissimilatory sulfate reducing bacteria have been identified as a source of pyrite in mineral deposit transformation (8). Pyrite is formed in nature from the reduction of sulfates or oxidation of H_2S. The elemental sulfur and the hydrogen sulfide can react with soluble metals to form the insoluble metal sulfides. The microbially mediated iron cycle presented in Figure 2. further summarizes the oxidation and reduction reactions that are catalyzed by bacteria.

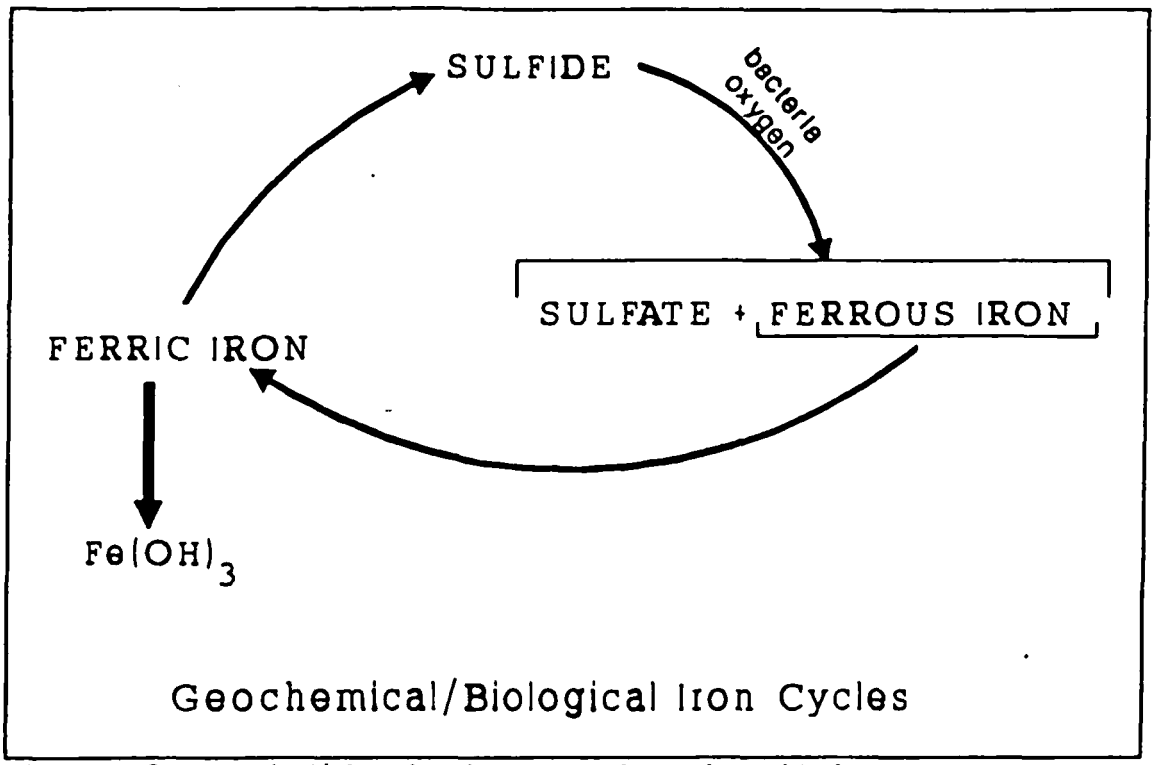

Figure 2. Geochemical/biological iron cycles in pyrite oxidation

In addition to T. ferrooxidans and T. thiooxidans, a number of other bacteria have been implicated in the biological decomposition of various mineral sulfides and in the solubilization of metals. The iron bacteria T. ferrooxidans, T. thiooxidans and the Ferrobacilli have proven effective in tank leaching of gold ores and ore concentrates (9,10) and have been used in copper dump leaching (11). Other bacteria that have been found in association with sulfide ores include T. thioparus, T. perometabolis, T. denitrificans, T. neapolitanus, Arthrobacter and Chromatium (12). Growth characteristics are listed in Table I. for select bacteria identified with sulfide transformations. These bacteria show a wide range of growth conditions they can operate in and demonstrate the extensive assortment of bacteria that could be involved in sulfide ore transformation.

Table I. Sulfide Ore Bacteria, Growth Conditions

microorganism	pH	temp., °C	aerobic	nutrition
Thiobacillus thioparus	4.5-10	10-37	+	autotrophic
T. ferrooxidans	0.5-6.0	15-25	+	"
T. thiooxidans	0.5-6.0	10-37	+	"
T. neapolitānus	3.0-8.5	8-37	+	"
T. denitrificans	4.0-9.5	10-37	+/-	"
T. novellus	5.0-9.2	25-35	+	"
T. intermedius	1.9-7.0	25-35	+	"
T. perometabolis	2.8-6.8	25-35	+	"
Sulfolobus acidocalderius	2.0-5.0	55-85	+	"
Desulfovibrio desulfuricans	5.0-9.0	10-45	-	heterotrophic

Although many of these bacteria are strictly aerobic, there are some microbes such as T. denitrificans that will act as a facultative anaerobe in anoxic conditions. The bacteria are capable of substituting iron, copper or even nitrate for oxygen as a terminal electron acceptor in the energy reactions of the cell. These reactions are defined for only a few microorganisms but raise the question about the role of other potential facultative anaerobes in the transformation of ore deposits.

The main point in identifying these microbial associations with sulfide ores is that bacteria other than the most acidophilic strains probably have some small role to play in ore oxidation and transformation. Conditions in many ore deposits are such that these bacteria apparently exist in only small numbers or less viable populations. The key to using these bacteria in biohydrometallurgical processes is then the adaptation to an ore and augmentation of the population to carry out specific leaching goals. Each ore will present very specific leaching problems but there is evidence that bacteria other than the Thiobacilli can be effective in mineral leaching (13). This broadens the range of conditions for bacterial leaching and shows increased promise for design of fixed-bed reactor bioleaching programs. Even though ore specific leaching problems preclude the use of generic populations, bio-engineered solutions in bacteria population design should be possible for many ore types.

Tank Bioleaching for Sulfide Ores

Tank bioleaching of sulfide ores and ore concentrates has been successfully demonstrated by several companies and is offered as an alternative to other refractory ore treatments such as roasting or pressure oxidation. Tank leaching presents economic and environmental advantages over these traditional processes for ore concentrates or high grade ores (14). With low to medium grade ores, though, the tank bioleaching processes are not as economically attractive. Reagent and energy costs eliminate very refractory, low grade ores from tank bioleaching and process control and recovery problems preclude heap leaching at the present time.

The fundamental principal involved in successful tank bioleaching is that the bioleaching is a pre-treatment step prior to conventional cyanide leaching. Solubilization of gold or silver during the bioleaching is not a goal of the bio-oxidation steps. There are indications that many ores do not need a homogeneous dissolution of the sulfides to effect a successful cyanide leach (15, 16). The tank bioleach process detailed in Figure 3. takes from 24 hours to several days depending on the ore and the pulp densities. The most efficient tank leaches use T. ferrooxidans that have been grown to a working concentration separately from the ore and are then added with nutrients for the bioleach process. The growth requirements of Thiobacillus ferrooxidans are the best defined for all of the Thiobacilli and the bacteria are ubiquitous in processed sulfide ores (17), mine drainage solutions and many transition zone ores.

Tank bioleaching technology can typically improve gold recoveries to 85 to 95% total recovery. Process control of pH and temperature can effect the economy of the process or its workability in some environments. One of the advantages of the tank bioleaching is that it allows for close control of pH and temperatures that would be impossible to control in a heap leach situation.

Bioleaching with an optimized tank design was originally conceived as an improvement to conditions for leaching precious metals. Leaching in natural reactor systems (dump leaching) is an effective process for base metal recovery systems but is not acceptable for precious metal leaching circuits. Tank designs used effectively in different processes include continuously stirred tank reactors or cascade reactor systems for continuous processing. Both batch and continuous processes are possible with an upper limit of a 10 to 20 tpd capacity (18).

Other options for microbial pre-treatment of ores in tank leaching operations include the use of thermophilic microorganisms or elevated pressures to enhance bioleaching rates (19,20,21). While most of the research using thermophiles such as Sulfolobus acidocalderius has been for copper extraction, these microorganisms should have the same potentials for heap or tank bio-oxidation of precious metals. The advantage of using a balanced population of mesophilic and thermophilic microorganisms is that each population would be variably active depending upon temperatures within a tank leach or a heap leach. The balanced population concept would eliminate the need for the strict temperature control necessary for very specialized leaching populations.

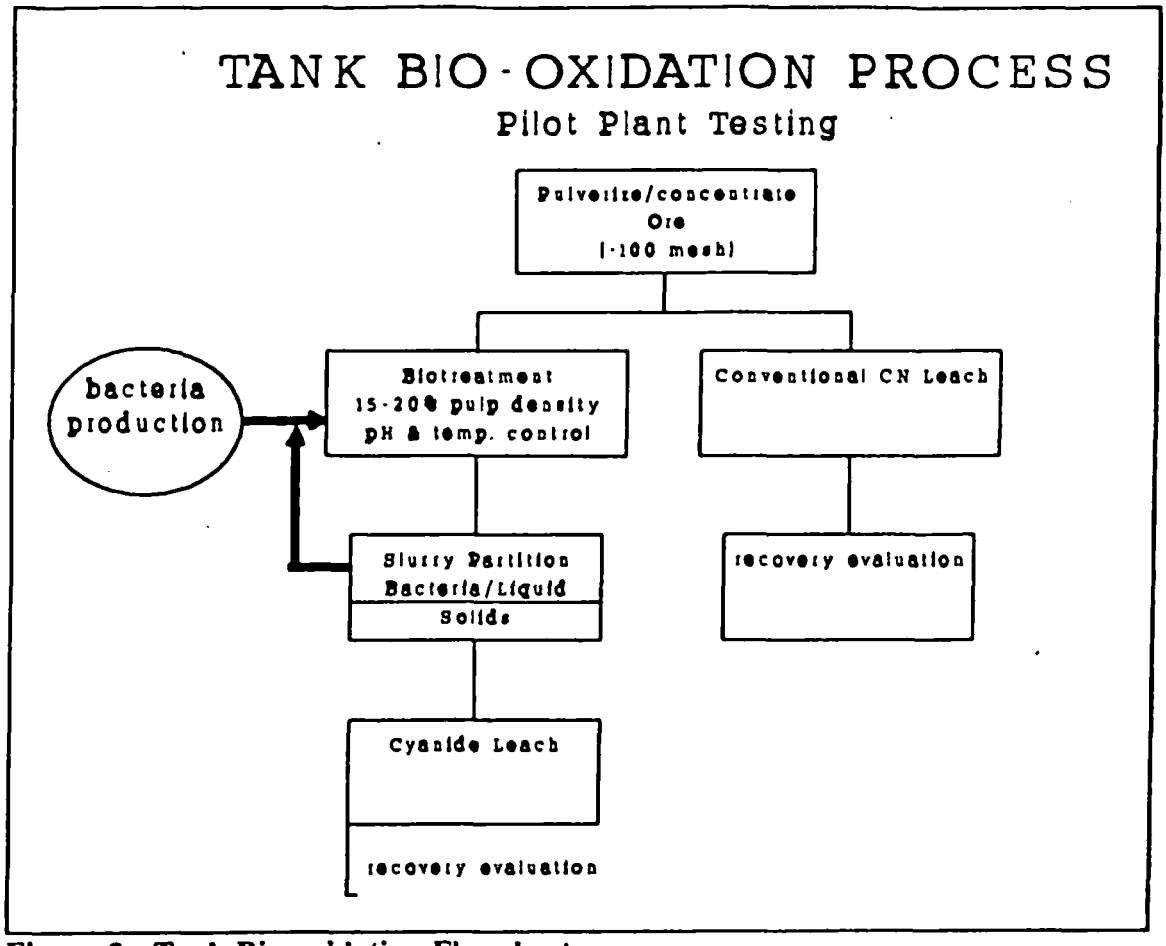

Figure 3. Tank Bio-oxidation Flowchart

Heap Leaching with Bacteria

The development of a bio-oxidation process for heap leaching of sulfide ores is a combination of bacteria selection/adaptation and process operation design. It is clear that bioleaching or bio-oxidation processes occur naturally within ore deposits and processed ores and that microbial pre-treatment of ores has proven to be effective in tank leaching methods. In any in situ treatment, however, there are additional limiting factors controlling the process design. The problems to be solved in bioleaching design for column or heap leaching include bacteria selection and adaptation, temperature control and pH control. Metal-hydroxide precipitates and other reaction by-products can form an insoluble coating on a sulfide surface. Formation of any protective reaction products on the sulfide surface can inhibit further bioleaching or subsequent cyanide leaching. Nutrient requirements and possible toxic species in the ore must also be identified in preliminary research.

The first step in the bio-oxidation process design is the isolation and adaptation of the bioleaching population. Bacteria can be isolated directly from the ores or adapted from existing populations. Adaptation to the ore includes growth of the bacteria in chemically defined media and also in ore infusion media. These techniques assure that the leaching population will be both tolerant of possible toxic components in the ore and also able to use the ore as a nutrient source for sulfur and iron. At this development stage, information from flask adaptation and leaching tests can identify metal and reaction by-product solubilization.

The portion of a population native to the ore that will actually participate in the bio-oxidation of the ore can be a very small percentage of the total population. The non-working portion of the population can competitively inhibit the sulfide oxidizing bacteria to the point where the sulfide decomposing strains may be unable to have any significant impact on the bio-oxidation. For this reason, the adaptation/augmentation process must be done for each ore-specific leaching problem. Each specialized population may also require distinctive nutrients which can be identified at this stage of the process research.

A bioaugmentation of the working population is accomplished by selective separation and culturing techniques. The end result of a successful bioaugmentation is a strain of working bacteria that has been selectively enhanced for each ore-specific leaching problem. This working strain can be ideally balanced with bacteria that can either extend the working life of the bio-oxidation bacteria, or be effective under different environmental conditions. The perfectly balanced bio-oxidation strain would contain bacteria that acted as:

1. Primary bioleaching bacteria
2. Secondary strains to remove rate-limiting by-products.
3. Secondary bioleaching strains active at different pH ranges.
4. Secondary bioleaching strains active at elevated temperatures.

This ideal, working population would then be grown separately from the ore in an optimized nutrient media and inoculated on the ore when log phase growth had been reached. This separate growth technique insures that sufficient numbers of working bacteria will be available for the bio-oxidation processes and will not be dependent upon generation of the working population in the ore. Biostimulation techniques where native bacteria are activated by nutrient addition can also be effective in some situations and offers the advantage of eliminating the time-consuming isolation and augmentation methods. The bioaugmentation techniques, however, appear at this time to have the best potential for development of heap leach bio-oxidation technology.

The final problem to deal with in each specialized population development sequence is the tendency of bacteria to mutate and change carefully engineered metabolic characteristics.

Bacteria are generally susceptible to enzymatic re-orientation caused by any alteration of their environment. This can mean that the metabolic characteristics that allow the bacteria to perform successful bioleaching can abruptly change when inoculated on the ore or for obscure reasons during the bio-oxidation process. There is no perfect way to control this problem but it can be mitigated by careful preservation of the working strains as back-up. Growth of the bacteria to concentrations significantly greater than those necessary for optimal bioleaching can also dilute the effects of random mutations and changes in the working strains.

The test series for successful bioleaching includes:

1. Tank leaches under carefully controlled conditions to define bacteria growth characteristics and changes, metal solubilization, by-product formation and leaching efficiencies.

2. Column leaches to predict field performance of working bacteria under less controlled conditions with larger sulfide ore fractions.

3. Pilot heap leaches to determine the actual field performance of the bioaugmented bacteria.

Each test stage allows for process adjustment including additions of new bacteria, optimized bioleaching contact times and field re-culturing of large quantities of the working bacteria. It is also possible that selected wash cycles might be necessary to remove bioleaching metabolic by- products or to kill the bacteria at the end of the bio-oxidation cycle. Many of the bacteria that have a potential for sulfide bioleaching can also have a negative impact on cyanide consumption during the cyanide leach cycle.

The research template detailed in Figure 4 summarizes the process development scheme for isolation and adaptation of the bio-oxidation bacteria.

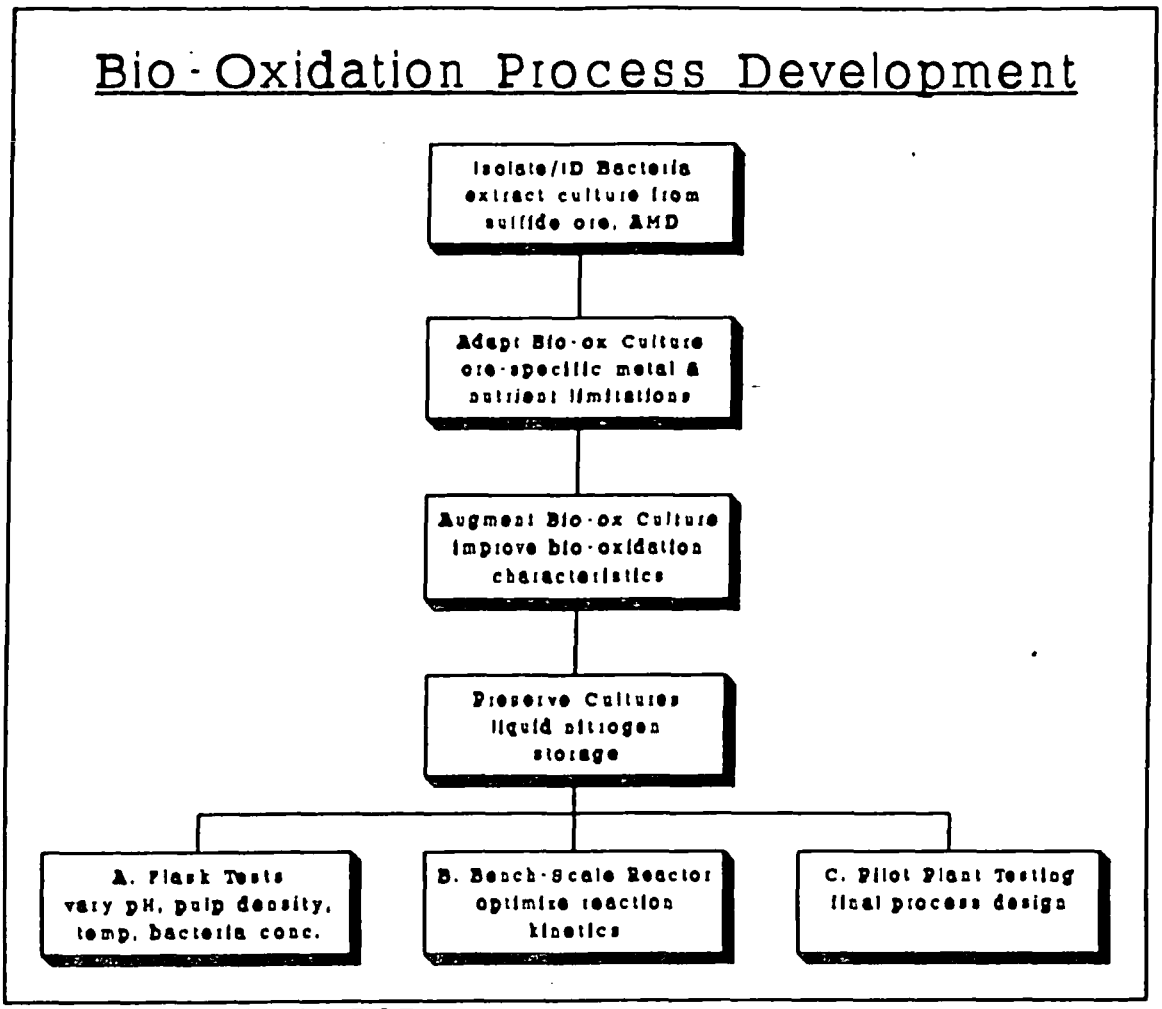

Figure 4. Bio-oxidation R&D

Conclusions

Bio-extractive metallurgy is a technique that will be necessary to the development of many sulfide ore reserves now and in the future. Bacterial oxidations have proven to be useful in dump recovery operations as well as tank leaching for gold and silver. The techniques offer some economic and environmental advantages over traditional processes but need to be further developed to have an impact on gold recovery in low grade sulfide ores. The key to this development will come through biotechnology improvements using bioaugmentation engineering processes.

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Chapter 34

New Technologies for Mining Waste Management

Biotreatment Processes for Cyanide, Nitrates and Heavy Metals

L.C. Thompson and R.L. Gerteis

Abstract

Cyanide, nitrates and heavy metals are by-products of mining and recovery operations that have the potential to influence soil, surface water, groundwater and air quality. Natural bacteria treatment processes were developed and tested for cyanide decomposition, denitrification and metal re-mineralization in leached ore residues and groundwater. Bench-scale lab tests and field testwork demonstrated the efficiency of microbial treatments for *In Situ* remediation of ore residue and process solutions.

Introduction

Precious metal heap leaching technology has developed in the United States since the late 1960's and with the rise in gold prices is responsible for the rapid increase in gold production in this country. The economy of heap leaching is based upon a closed-circuit design in which dilute cyanide process solutions are continuously recycled. Little or no effluent is discharged to the environment. Despite the low environmental impact of most plant operations, some wastes may require treatment of residual cyanide, nitrate and heavy metals. The development of novel treatment and waste management procedures has been encouraged by responsible business practices and increasingly conservative regulatory policies. Biotreatment of cyanide and heavy metals in solid and aqueous wastes are some of the most promising of the new treatment technologies.

After metals have been extracted from ore in a cyanide heap leach, ore residues are washed to remove most of the remaining cyanide and precious metals. Cyanide exists as three basic complex forms in a leached ore residue. Hydrogen cyanide, the most unstable form, can exist in ionic form in solution only at an elevated pH. Easily dissociable metal-cyanides, such as zinc cyanide, will naturally degrade through a variety of chemical, physical and biological processes. Ferrocyanides, cobalt and gold cyanide compounds, the strongly complexed metal-cyanides, are extremely stable in nature and can persist in aqueous and solid matrices (Towill, et al). Natural volatilization, attenuation and decomposition can be expected to remove most of the easily dissociable cyanides from a solid ore residue. The small amount of cyanide remaining will be the more stable metal-cyanides and these complexes may exhibit a longer-term stability.

Current cyanide waste mitigation technology emphasizes the treatment of aqueous wastes through chemical or biological methodologies. The chemical treatments for cyanide include oxidation processes such as hydrogen peroxide treatment, ozonation, alkaline chlorination or sulfur dioxide treatment (Huiatt, et al). Other approaches for cyanide removal consist of various adsorption, precipitation or electrolytic procedures. The main disadvantages of these traditional treatment methods are that:

1) Chemical remediation processes can be costly.
2) Conventional chemical treatents are only partially effective for total cyanide treatment.
3) Treatment can replace the cyanide with another undesirable pollutant.
4) Most remediation is designed mainly for treatment of aqueous-based waste forms.

Possible advantages of bioremediation are that treatment can be more cost effective and complete treatment of complexed cyanide is achieved. Tracer studies have determined that the by-products of microbial cyanide decomposition reactions (Miller and Orgel) are natural and non-toxic. Denitrification end-products are also non-toxic (Cooper and Smith) and the result of bacterial metal accumulation is immobilization/biomineralization of soluble metals (Lowenstam and Weiner).

Bacteria have been used in general aqueous waste treatment for over 50 years (Johnson, et al). In a municipal or agricultural waste treatment system, bacteria can degrade many organic wastes to harmless by-products through normal cellular metabolic reactions. The complexity, concentration and potential high toxicity of cyanide waste forms, however, often preclude the use of natural bacteria treatment methods. Using bacteria for biodegradation of cyanide wastes from electroplating

operations was proposed as early as 1956 (Pettet and Mills). The mining industry in both the Soviet Union (Grableva and Ilyaletdinov, et al) and the USA (Mudder and Whitlock, 1984) has developed microbial treatment schemes for cyanidation wastewaters. In microbial cyanide decomposition, cyanide is used by the treatment bacteria as a carbon and/or nitrogen source for cell metabolic processes.

The main goals of this research and testing program were to:

1. Isolate bacteria that were tolerant to high concentrations of cyanide.
2. Identify bacteria with the natural ability to use cyanide compounds or nitrate as a source of nutrients.
3. Stress native populations of cyanide-tolerant bacteria in chemically defined broths to enhance the natural cyanide-degradation abilities.
4. Demonstrate the cyanide biodecomposition and denitrification potential of the lab-enhanced bacteria in controlled tests for both aqueous and solid cyanide-containing wastes.
5. Evaluate biotreatment costs and efficiencies for solid waste remediation.

Experimental

Cyanide Biotreatment

A biotreatment program was developed in the lab and field tested for removal of total cyanide and nitrate in solid ore residue and leachate solutions. The test approach is outlined in Figure 1 and included experiments for biotreatment of leached ore residue, process solutions and groundwater.

Although volatilization, complexation and adsorption are the predominant mechanisms of cyanide removal, biological elimination of cyanide could be a significant factor in ore residue or soil treatment. Cyanide metabolism is known to occur naturally in many bacteria and fungi (Knowles). Soil bacteria and pathogenic fungi are also found near cyanogenic species of plants which indicates microbial tolerance to cyanide if not cyanide decomposition capacity (Fry and Myers). Bacteria that have been implicated in cyanide decomposition include diverse species of the genera Pseudomonas (Mudder and Whitlock), Bacillus (Castric and Strobel), Thiobacillus (Buchanon and Gibbons), some cyanobacteria (Ponomareva, et al), mixed populations (Grableva, et al), and Actinomycetes(Harris and Knowles).

Laboratory studies using labeled potassium cyanide have shown that bacteria will use the carbon or nitrogen from the cyanide. Cyanide components form asparagine, aspartic acid, carbon dioxide and intermediates such as ß-cyanoalanine, α-amino butyronitrile, amino acids and formamide or formic acid (Castric). Most of the types of bacteria capable of demonstrating cyanide metabolism are found in surface waters or soils that contain some organic matter for nutrient sources. The diversity of bacteria using cyanide suggests that the chances are good for finding bacteria specific for cyanide decomposition in arid soils or leached ore residue.

Bacterial use of cyanide compounds depends on environmental factors such as site geochemistry, bacteria concentration and the native types found in cyanide environments. Some characteristics of soil or ore residue that may have an impact on the viability of natural treatment bacteria are:

a.) nutrient limitation;
b.) the presence of toxic metals;
c.) oxygen concentration.

Microbial assays of cyanide-leached mining residue were conducted to determine presence of bacteria at different concentrations of total cyanide in the residue. Freshly leached and water-washed residue typically has 100-150 mg total cyanide per kilogram of residue. Bacteria were found to be established only when total cyanide values had dropped to less than 30 mg/kg total cyanide through natural attenuation and removal mechanisms. The bacteria found in this older residue were identified as a mixed population of both spore-forming and non-spore forming bacteria. Bacilli, Thiobacilli and Actinomyces were specifically identified as showing promise for cyanide biodegradation and metal tolerance.

Samples of all three types of bacteria were cultured in enrichment media with up to 100 mg/L cyanide (as a sodium cyanide). A culture provisionally identified as a mixed Bacillus population showed some promise in both cyanide tolerance and degradation after serial subculture in a Bacillus isolation/sodium cyanide broth. This culture, however, was not as active in bench-scale tests with leached ore residue.

A mixed population of native bacteria was isolated from a sulfide ore residue and subcultured for cyanide tolerance and degradation. After cyanide stress and subculture in a medium designed to approximate residue dump conditions, a population was found that had significant cyanide degradation potential. A comparison between native bacteria and biologically augmented populations for cyanide decomposition is shown in Figure 2.

The purpose of lab augmentation is to eliminate portions of the population that do not contribute to cyanide decomposition. The active cyanide decomposing bacteria can be a quantitatively small fraction of the total bacteria. Augmentation and stress tests eliminate

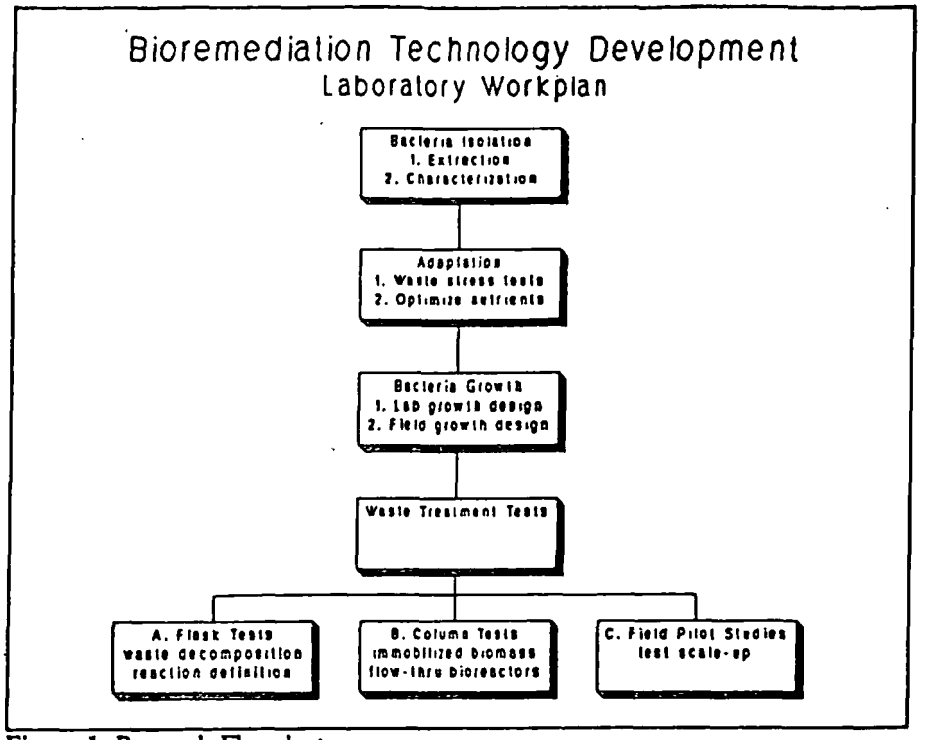

Figure 1. Research Flowchart

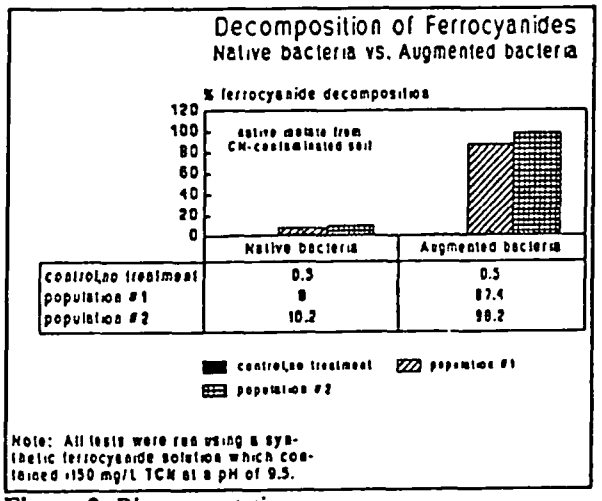

Figure 2. Bioaugmentation

non-working bacteria that can competitively inhibit the cyanide-oxidizing microbes. Bioaugmentation also exploits randomly induced mutations beneficial to cyanide biodecomposition.

To test the microbial cyanide decomposition, a series of flask tests, column tests, a 1500 ton and a 20,000 ton field test were designed. The flask tests used a 500 gram sample of minus 10 mesh ore residue. Column studies were run with 100 kg of minus 3/4 inch residue

packed in 6" x 10' PVC columns. The 1500 ton field test used minus 3/4 inch residue stacked 16 feet high on an impermeable liner. The 20,000 ton field test was run in a controlled area of a residue dump. Test areas were marked off to study effects of natural weathering, water washing, bacteria washing and direct bacteria injection. Results are presented in Table I for bench-scale testing and Table II for the column tests. Figures 3 and 4 compare cyanide decomposition between control and biotreatments in the field pilot tests.

Table I. Bench-scale Cyanide Biodecomposition

Flask Cyanide Decomposition

Flask ID	total CN, mg/kg test start 0 hours	total CN, mg/kg test end 48 hours	% CN removed chem/physical decomposition	% CN removed biodecomposition
#1, OR-4 bacteria	123.	<0.1	50-60	40-50
#2, " "	135.	0.9	50-60	40-50
#3, " "	130.	0.4	50-60	40-50
control, Sterile H_2O	117.	53.0	54.7	<1

Experiment Design: 500g of a -10 mesh leached ore residue were inoculated with 20 mL of treatment bacteria solution or sterile deionized water. Flasks were incubated at 21°C for 48 hours. Total cyanide in leached ore residue was determined by extraction in 5% NaOH and a reflux acid distillation. Residue pH = 8.9, treatment solution or water pH adjusted to 9.0

Note: Chemical and physical decomposition remove free and easily dissociable metal cyanides.

Table II. Column Tests - Cyanide Biodecomposition

Column Tests - Cyanide Biodecomposition

Column ID	total CN mg/kg start, Day 0	total CN mg/kg end, day 21	% decomp
#1, OR-2 bacteria	125	<0.1	99.9
#2, " "	119	0.5	99.6
#3, " "	130	<0.1	99.9
#4, " "	108	0.2	99.8
#5, control (H_2O wash)	127	49.3	61.2
#6, control "	131	57.0	56.5

For each test 100 kg of a fresh leached ore residue was loaded into a 6"x10" vertical PVC column. One pore volume of bacteria solution or sterile deionized water were applied in a percolation leach. Ore residue was tested for total cyanide by extracting with 5% NaOH and distillation of extracts in a reflux acid distillation.

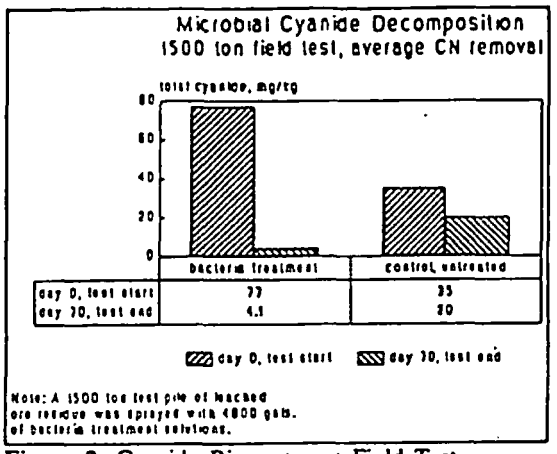

Figure 3. Cyanide Biotreatment Field Test

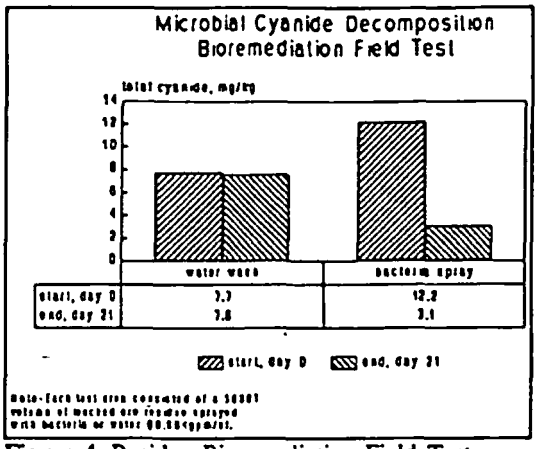

Figure 4. Residue Bioremediation Field Test

Microbial Denitrification

Nitrates can be found in ore residue as a result of nitric acid used in recovery operations. They are a very mobile residue component that can leach into soil and groundwater during washing operations or natural precipitation. Nitrates are regulated because they can be toxic to warm blooded animals under conditions that favor nitrate reduction to nitrite. Nitrite, in the bloodstream, reacts with hemoglobin to form methemoglobin with consequent disruption of oxygen transport in respiratory pathways (Lehninger). These reactions are of particular concern for infants. Nitrates may also react with secondary amines in the gastrointestinal tract to form carcinogenic N-nitrosoamines (Clesceri et al). Recommended levels of nitrate nitrogen in drinking water are therefore, usually less than 10 mg/L and nitrite nitrogen at less than 1mg/L (Faust and Aly).

Nitrogen, an essential nutrient for all living cells, is present as a component of proteins or nucleic acids in the cell. Some bacteria have evolved the ability to obtain nitrogen from nitrates for exothermic reactions or for assimilatory processes. The dominant use of the denitrification sequence by the cell is as an energy-yielding process (Payne).

Denitrification is regulated by the presence of the enzyme nitrate reductase in the cell. Its production in the cell can be stimulated by an environment low in oxygen or repressed by elevated oxygen tensions. The mechanism of reduction is the enzymatic mediation of the nitrate reduction to nitrite using a cytochrome b as the electron donor. The reaction sequence shown in Figure 5 indicates that end-products of denitrification are gaseous and are lost to the system.

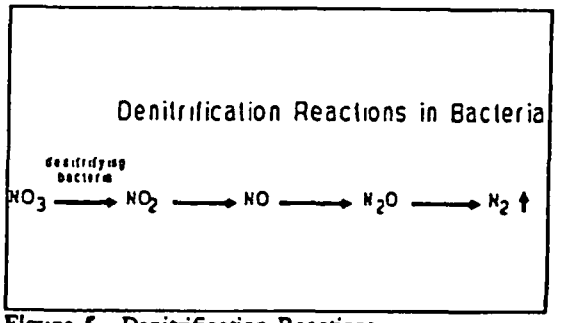

Figure 5. Denitrification Reactions

The bacteria chosen for denitrification tests included the augmented cyanooxidans population and pure type cultures of known denitrifying bacteria. Bench-scale tests were run on wastewater solutions in the lab. The most successful population was developed for field test work in the 20,000 ton pilot program for leached ore residue treatment.

Results of lab and field denitrification studies are shown in Figure 6 and 7.

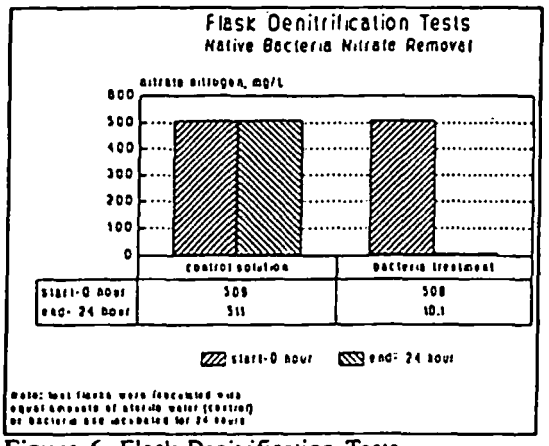

Figure 6. Flask Denitrification Tests

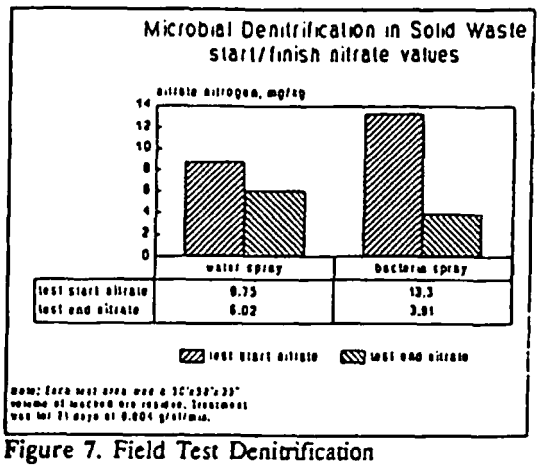

Figure 7. Field Test Denitrification

Microbial Metal Sequestering

Heavy metals form a significant portion of the pollutants found in toxic waste dumps and are increasingly present in our industrial wastewaters and natural surface and ground waters. Biological methods for concentrating metals from waste streams are receiving attention as natural process alternatives to traditional removal methods. Several processes using living and non-living bacteria for metal accumulation have been developed in recent years.

The conventional technology for treatment of metal waste streams includes physical and chemical processes where metals are immobilized or recovered. Treatment processes include hydroxide precipitation, chemical oxidation or reduction, evaporation, ion exchange, ultrafiltration, electrolysis or electrocoagulation reactions-(Cushnie). Many of these processes are costly and are not a complete solution to the problem of environmentally acceptable metal disposal. Recycling efforts, including using bacteria to concentrate metals, are receiving new attention because of high costs and long term liabilities associated with traditional treatment and disposal methods.

Numerous species of bacteria, fungi and yeasts are capable of accumulating several times their weight in heavy metals. Bacteria have been adapted to remove soluble metals from waste streams containing large amounts of metals such as gold, silver, chromium, cadmium, copper, lead, zinc, cobalt and others (Eccles and Hunt). There are two basic mechanisms involved in the metal uptake by bacteria (Starr et al):

1. Accumulation by surface binding to the bacterial cell wall or extracellular metabolic materials. The surface binding mechanisms include:
    - complexation of metals with organic compounds;
    - precipitation caused by ion exchange or production of oxalic acid in the cell;
    - chelation by cell membrane components such as pigments, phenolic polymers, cellulosic ligands or chitin.
    - remineralization of metal species as a result of complex interaction with extracellular products of bacterial metabolism.
2. Uptake into the cell for use in metabolic processes as necessary nutrients.

Surface binding and extracellular complexation mechanisms are capable of accumulating the largest amount of metals from solution(Fenchel and Blackburn). Intracellular uptake is typically responsible for a minor contribution to overall metal removal.

Metal accumulation was not a primary goal of this research but it was important to prove that metals would not be mobilized as a result of bacterial treatment of cyanide and nitrates. Results of lab bioaugmentation of native bacteria and bench scale tests are shown in Figures 8 and 9.

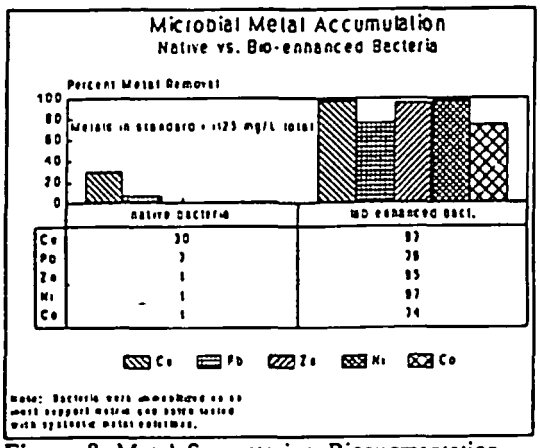

Figure 8. Metal Sequestering Bioaugmentation

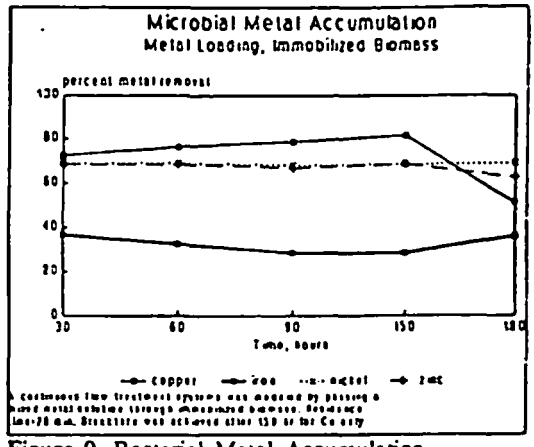

Figure 9. Bacterial Metal Accumulation

Conclusions

During the research program natural biotreatment bacteria were isolated and adapted to the ore residue. Field pilot tests, following successful bench scale testing, significantly decreased both total cyanide and nitrate concentrations in leached ore residue or treated solutions. By-products of bacterial cyanide and nitrate metabolism were determined to be natural and non-toxic.

The use of bacteria or fungi for removing heavy metals from waste streams is a rapidly developing technology that also may find application in the mining industry. Live bacteria, immobilized biomass and certain algae have all shown a good potential for selective metal removal from waste streams. At least one commercial process is currently available for metal waste remediation. Biological concentration or re-mineralization of metals may offer a low-cost treatment alternative for large volumes of contaminated groundwater or process water from mining, milling or ore beneficiation operations. Used alone or in conjunction with other treatment technologies, bioremediation of waste metals may provide a means of mitigating both high and low hazard waste streams.

The degree to which there will be a need for novel treatment methods for wastes from mining operations has not yet been determined. When waste remediation is required, however, biotreatment technologies should be considered. Innovative microbial programs appear to have many environmental and economic advantages over conventional treatment processes.

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Biological Field Treatment Applications in Gold Heap Leach Closures

Leslie C. Thompson

Background

The heap leach process used for recovering gold from oxide and sulfide ores is operated as a closed circuit system in which the cyanide process solutions are continuously recycled. In a well-designed operation there is little or no discharge of cyanide to the environment. Spent leached ore residues are water washed to remove most of the trace cyanides and precious metals remaining after completion of cyanide leaching. After the washing step, small amounts of cyanide, metal-cyanide complexes and nitrates remain in the residue. Most of the cyanide and nitrate residue constituents exist in the pore water of the spent ore rather than in the solid mineral fraction.

More than 90% of the complexed cyanides in a freshly washed ore residue are present as free cyanide or weakly complexed metal-cyanides. Natural volatilization and decomposition rapidly remove most of these easily dissociable cyanides from the spent ore. Only the stable, strongly complexed metal-cyanides, such as gold, cobalt or the ferrocyanides and other constituents such as nitrates have a long term persistence in the spent ore residue (Towill et al).

Despite washing and natural removal mechanisms, spent ore has the potential to act as a point source of complexed cyanides and nitrates for soil and groundwater contamination if inadequately contained (Huiatt et al). The groundwater contamination is caused by the leaching of the soluble cyanide compounds and nitrates from the pore water of the residue.

One of the possibilities for mitigation of the point source of complexed cyanides and nitrates is a biological treatment of the residue. The biological treatment is designed to degrade metal-cyanide compounds and nitrates in the spent ore. A biological treatment system uses naturally occurring bacteria that have been enhanced in the laboratory to decompose metal-cyanide compounds and nitrates. The by-products from this microbial treatment system are natural and nontoxic.

Cyanide metabolism is known to occur in many bacteria and fungi (Knowles). Bacteria that have been implicated in cyanide decomposition include diverse species of the genera Pseudomonas (Mudder and Whitlock), Bacillus (Castric and Strobel), Thiobacillus (Buchanon and Gibbons), some cyanobacteria (Ponomareva, et al), mixed populations (Grableva, et al), and Actinomycetes(Harris and Knowles). Bacteria basic cell metabolic processes. The efficient use of cyanide as a nutrient source depends on environmental factors such as site geochemistry, bacteria concentration, nutrient limitation, other toxins and the oxygen concentration.

Nitrogen is an essential nutrient for all living cells and is present as a component of proteins or nucleic acids in the cell. Some bacteria obtain nitrogen from nitrates for exothermic reactions or for assimilatory processes (Payne). Denitrification is regulated by the presence of the enzyme nitrate reductase in the cell. Its production in the cell can be stimulated by an environment low in oxygen or repressed by elevated oxygen tensions. The mechanism of denitrification is the enzymatic mediation of the nitrate reduction to nitrite using a cytochrome b as the electron donor. The end-products of denitrification are gaseous and are lost to the system.

The purpose of the laboratory and field tests was to evaluate the possibility of using an *in situ* biological treatment method for solid spent ore residues.
The specific goals of the lab and field tests were to:

- Isolate and augment native bacteria that possessed the potential to act as a natural cyanide-decomposition and denitrification population,
- Test the cyanide biodecomposition potential of lab-produced bacteria in cyanide-leached ore residue,
- Measure the denitrification capacity of the same bacteria in a solid residue matrix,
- Use the test data to complete a cost and engineering study for mitigation options for a spent ore dump.

Definition of Bioremediation

Bacteria have been used for treatment of organic wastes in municipal and agricultural waste treatment plants for over 50 years (Johnson et al). In these treatment systems, bacteria that are native to the waste or treatment plant are

used to naturally degrade the organic waste material to harmless by-products. Until recently though, the concentration, complexity and high toxicity of many inorganic industrial wastes has excluded them from natural biological treatment. Biotechnology and bio-engineering research has made biological remediation of industrial wastes a viable treatment technology.

Bioremediation techniques are defined as the use of natural or biologically augmented bacteria to remove or decompose an undesirable component which occurs in groundwater, surface water or soil. The undesirable components can be any manufactured, transformed or naturally occurring substances which can have a detrimental effect (real or perceived) on man or his environment. The key to successful biotreatment of industrial wastes is the discovery and adaptation of bacteria that are specific for biochemical degradation of each particular waste stream.

Reversal of contamination requires the elimination of the point sources of the undesirable components, as well as, renovation of the waste source and resource reclamation. Biotreatment technologies offer an enhanced, natural solution to removal of complex wastes such as metal-cyanides and nitrates.

Bacteria source - Isolation and Augmentation

To develop an *in situ* microbial treatment for cyanide and nitrate trace contaminants, several strains of bacteria were isolated from a spent ore. These native bacteria were cultured and stressed in chemically defined broths to enhance any potential that they might have for natural decomposition of cyanide complexes and nitrates. Stressing the working populations also eliminated the non-working bacteria that could competitively inhibit the biotreatment bacteria.

The development sequence for cyanide biodecomposition and denitrification is presented in Figure 1. The first step in microbial treatment of cyanides involved isolating bacteria from older leached ore residue. The assumption was that some of these native bacteria would be able to tolerate low concentrations of cyanide and perhaps be able to use cyanide to meet cellular metabolic needs.

The bacteria isolated from the leached ore residue were tested in bench-scale tests for decomposition of free cyanide and total cyanide as a potassium ferrocyanide complex. The initial test work showed that native bacteria isolated from the residue and grown in chemically defined media would decompose complexed cyanides a maximum of 30 to 50%. To further enhance the microbial cyanide decomposition potentials, the native bacteria were biologically augmented by specific culturing techniques and randomly induced mutations. Final flask and column tests indicated that a population had been developed that would remove up to 97% of the total, complexed cyanides.

Nitrates are a possible decomposition by-product of microbial cyanide metabolism and also exist in the residue as a processing product. The denitrifying bacteria were identified as native to the original cyanooxidans isolate and were selectively cultured and preserved for separate test work. They were included in all cyanide decomposition populations to remove any nitrates that might be formed as a result of cyanide metabolism by the bacteria.

Flask Biotreatment Studies - Cyanide Biodecomposition and Denitrification

Decomposition of cyanide complexes and nitrates by bacteria was tested in flask studies with both synthetic and spent ore leachate solutions. The purpose of the flask studies was to determine if the selected bacteria could perform denitrification or cyanide decomposition in a controlled situation.

The initial flask studies showed that an enhanced native strain of bacteria had been found that would remove 35 to 50% of the ferrocyanides from a synthetic solution at a pH of 8 to 11. Further stress and specific sub-culturing of the bacteria produced a population that would remove up to 99% of the ferrocyanide complexes from synthetic solutions.

Flask tests of microbial denitrification were run with synthetic nitrate solutions and water from a catchment basin for ore leachate solutions. The results of these flask tests indicated that three different strains of bacteria had been found that would biochemically denitrify the catchment pond solutions and nitrate synthetic solutions. The strain that showed the best denitrification potential was the same bacteria used for the microbial cyanide decomposition tests. These bacteria removed 92% of the nitrates in catchment pond water that contained over 110 mg/L nitrates at the test start. This strain also removed 99% of the nitrates the synthetic solution that contained 500 mg/L nitrates at the test start.

Column Studies - Cyanide Biodecomposition and Denitrification

Microbial decomposition of complexed cyanides and nitrates in leached ore residue was tested in column studies in the laboratory. The purpose of the column studies was to model cyanide biodecomposition and denitrification in a solid waste system. These tests served as a feasibility study for test expansion to field pilot programs. A total of six test columns were set up to test a percolation leach of spent ore with bacteria solutions. The spent ore was loaded into 6" x 10' PVC columns and percolation leached with 2.5 pore volumes of dilute bacteria solutions. The spent ore and the column effluent solutions were tested during and after the treatment for total cyanide and nitrates.

The results of the column studies showed that the residue that was leached with the bacteria solution indicated a

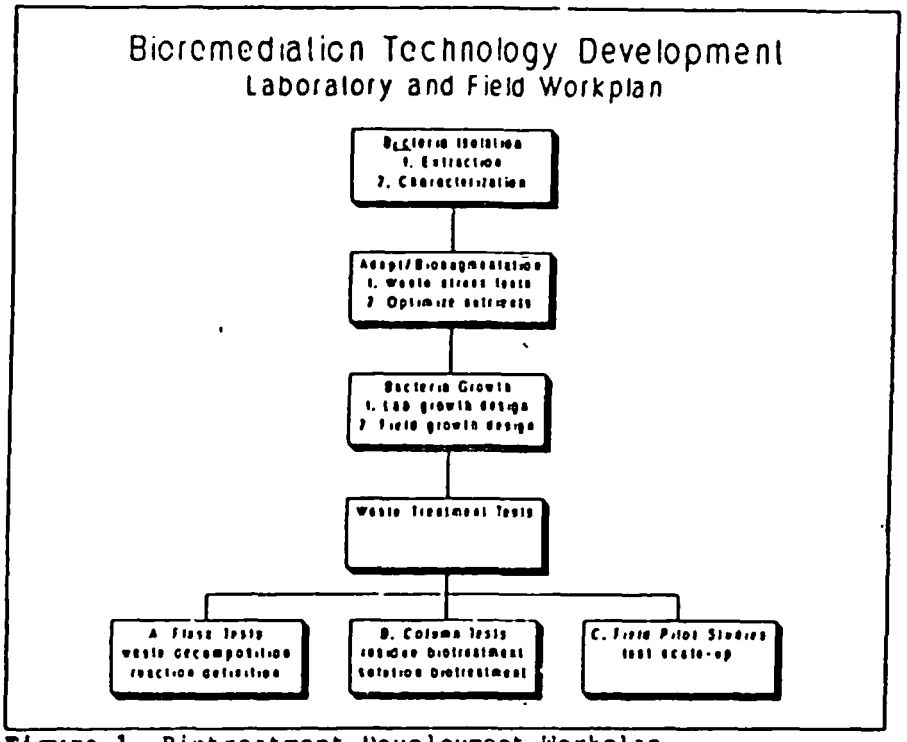

Figure 1. Biotreatment Development Workplan

total cyanide decomposition of 99% in both the solid residue and the leachate solutions. The control residue columns that were water washed at the same flow rates showed that there was a 92% removal of the cyanide complexes from the residue by washing effects but that there was only an 8% removal in the leachate solutions. These results indicated that a simple water wash of the residue would relocate but not decompose the soluble metal-cyanides.

The results of the denitrification column tests indicated that a 98% removal of the nitrate nitrogen was effected in the bacteria treated residue where the nitrates in the water-washed control were again washed out in leachate solutions but were not degraded.

Field Test Study Area

The study area for the field tests of bioremediation techniques was located in a select area of a spent ore dump at a mine in northern New Mexico. Four test pads were marked off on the surface of the dump and were located to avoid cross-contamination between test areas. The test area was chosen to have a residue depth to bedrock of 35 to 45 feet. The surface of each pad was 50 x 50 feet. The surface of each test pad was ripped to a depth of 20 inches to increase the surface permeability for test solutions.

The test pads were treated as follows for the course of the study:

- Test Pad #1 was not treated at all and served as a weathering control to monitor the natural decomposition and relocation of contaminants by natural forces.
- Test Pad #2 was sprayed with well water at a rate of 0.004 gpm/ft^2. This test pad served as a washing control to monitor decomposition and relocation of contaminants due to washing effects.
- Test Pad #3 was sprayed with a solution of well water and treatment bacteria. This test pad served to measure the effects of a biological remediation scheme using bacteria to decompose cyanides and nitrates in the residue.
- Test Pad #4 was injected with well water/bacteria solutions. This test pad served as a comparison with Test Pad #3 to assess possible UV sterilization of bacteria in spray applications.

Each test area was sampled at various depths to bedrock prior to the test start with a hollow stem auger, split spoon sampler. Residue samples were collected from each test pad at regular intervals throughout the course of the test and after the test was completed. Results of the sample analyses are presented in Figures 2, 3 and 4 for cyanide biodecomposition and in Figures 5, 6 and 7 for denitrification. Data from test

pads 2 and 3 are graphed as representative of the control compared to biotreatment.

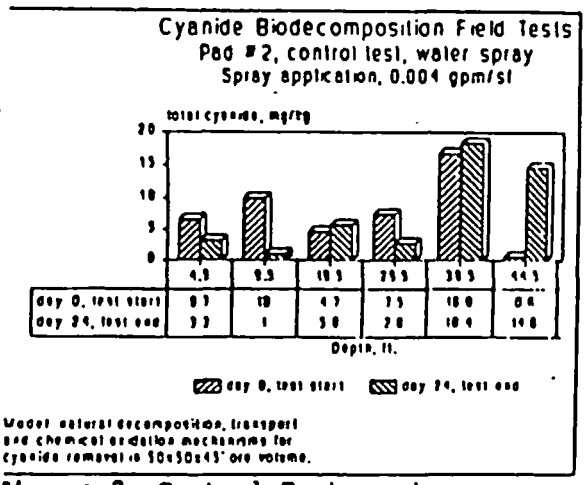

Figure 2. Control Test

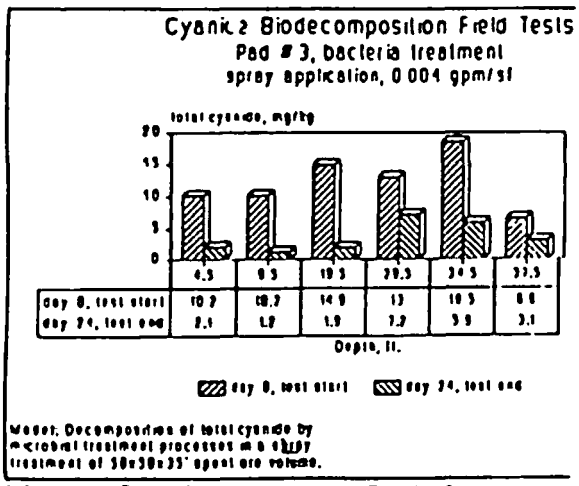

Figure 3. Biotreatment Test Area

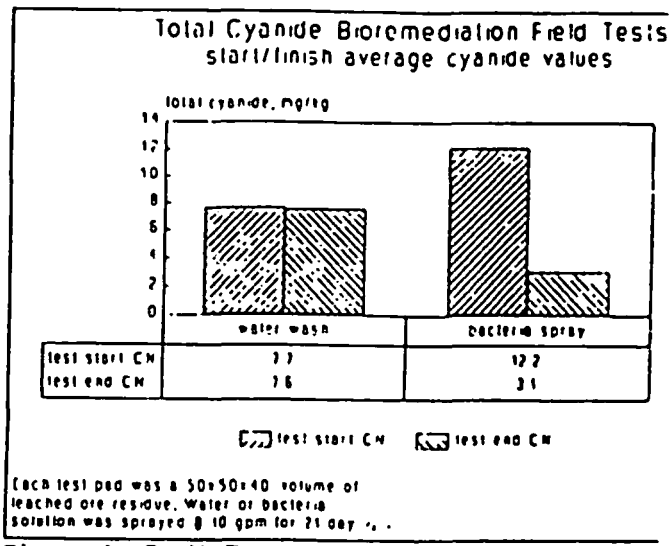

Figure 4. Cyanide Treatment Comparison

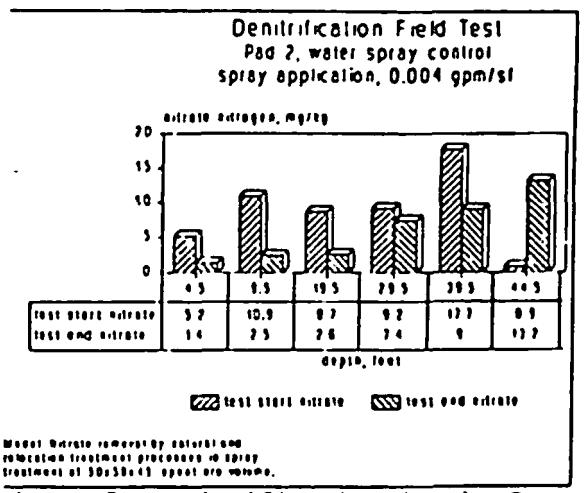

Figure 5. Denitrification in the Control Test Area

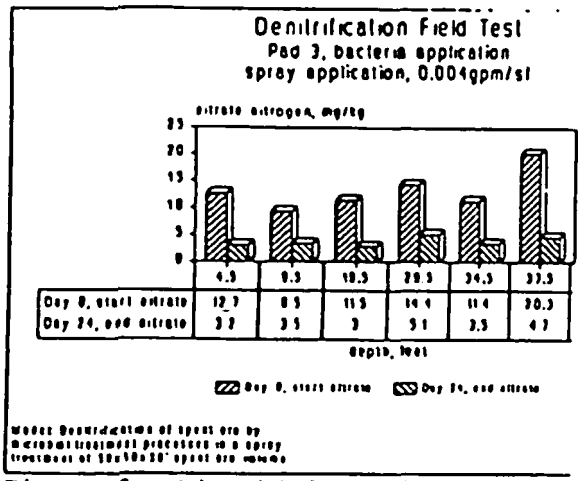

Figure 6. Microbial Denitrification Test Area

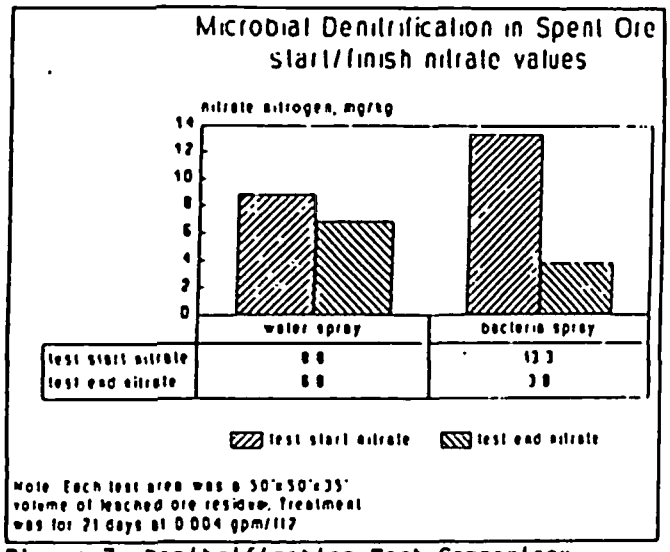

Figure 7. Denitrification Test Comparison

Data Evaluation

The field test results indicate that a water wash is effective in relocating the cyanide and nitrate contaminants from the upper layers of the spent ore to the lower layers. This type of treatment could be acceptable if the dilution was sufficient to reduce the total cyanide or nitrate concentration. The overall decomposition of both cyanide and nitrates in Figures 4 and 7 show that the water wash treatment only relocates the contaminants with no decomposition. The bacteria treatment seems to decompose the cyanide and nitrates rather than relocating them.

Both lab and field tests demonstrate that biological treatment processes can successfully treat mining wastes from gold ore processing. Increasingly conservative regulation of the mining industry demands development of innovative, cost-effective treatments for mine wastes. Biotreatment costs for cyanide and nitrate removal from process solutions, mill muck and spent ore should be less than competitive chemical treatments.

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PRODUCT AND SERVICE AGREEMENT
HECLA MINING, INC.
PHASE I AGREEMENT

Pintail Systems Inc. (hereafter "PSI"), and HECLA MINING, COMPANY INC. (hereafter referred to as "Client") agree as follows:

The term of this Agreement shall commence upon the date of execution by both parties and shall continue for four (4) months. The definition of work to be performed is contained in the Proposal prepared for Hecla Mining, Inc., Yellow Pine Unit, entitled Pilot Plant Test Program, Biotreatment of Cyanide in Heap Leach Spent Ore, Column Test Design (attached).

Charges for such services (Phase I) will be $22,810 payable in two (2) equal amounts. The first invoice will be rendered at the signing of this Agreement, the second invoice at the conclusion of the Agreement. Invoices will be due and payable within thirty (30) days of receipt of invoice. Payments made after the thirty (30) day period will be subject to a penalty interest at the rate of 12% per annum. Client shall, in addition, pay or reimburse PSI for all reasonable travel and lodging expenses in association with conducting this Agreement, federal, state, municipal or government excise, sales, use, occupational or like taxes in force or enacted in the future.

In order to perform hereunder, either party may find it beneficial to disclose to the other party specifications, drawings, discoveries, data, organisms, organism mixture, biological processes, computer programs, or documentation or other technical or business information (herein "Information) which the disclosing party considers proprietary.

Unless the disclosing party acknowledges to the contrary, all Information obtained by the other party hereunder will be presumed to be confidential and proprietary and will be so treated by the receiving party.

With respect to Information provided under this Agreement, the receiving party shall:

1. Hold the Information in confidence, and,
2. Restrict disclosure of the Information solely to those employees of the receiving party with a need-to-know, and not disclose it to any other parties, and,
3. Advise those employees of their obligations with respect to the Information, and
4. Use the Information only for the purposes hereunder, except as may otherwise be mutually agreed upon in writing.

The receiving party shall have no obligation to preserve the proprietary nature of any Information which:

1. Was previously known to the receiving party free of any obligation to keep it confidential, or,
2. Is disclosed to a third party by the disclosing party without restriction, or,
3. Is or becomes publicly available by other than unauthorized disclosure.

The Information shall be deemed to be the property of the disclosing party or its affiliates and upon request, the receiving party will return all Information in tangible form to the disclosing party or destroy all such Information.

Nothing contained in this Agreement shall be construed as granting or conferring any rights by license or otherwise in any Information disclosed.

In the course of conducting discussions, executing a contract, or providing Information PSI may disclose certain inventions, discoveries, improvements, procedures, ideas, research, organism mixtures, organisms, biological processes, and computer or other apparatus programs (collectively "Innovations") whether or not patentable, copyrightable or susceptible to other forms of protection. These Innovations may be conceived of or made by PSI and its employees prior to or in the course of performance of an activity with the Client and the Client agrees that PSI retains all rights, title and interest to such Innovations. The terms for disclosing Information set forth and agreed to in other sections of this document also apply to Innovations.

This Agreement shall benefit and be binding upon the parties hereto and their respective successors and assigns.

Notice which shall or may be given in writing and pursuant to this Agreement shall be given in writing and shall be sent to the other party at the address listed below by registered or certified mail, postage prepaid, return receipt requested. The date of the postmark shall be deemed to be the date on which such notice is given.

For PSI: David D. Gridley
President
Pintail Systems Inc.
6 Wilcox Street
Simsbury, CT 06070

For Client: Todd Fayram
Unit Manager
Hecla Mining, Inc.
Yellow Pine Unit
P.O. Box 75
Yellow Pine, ID 83677

All persons furnished by PSI or the Client, shall be considered solely employees or agents of the respective parties; and each party shall be responsible for compliance with the laws, rules and regulations involving, but not limited to, employment of labor, hours of labor, working conditions, payment of wages and payment of taxes, such as unemployment, social security and other payroll taxes, including applicable contributions from such persons when required by law as regards it.

Each of the parties will defend, indemnify and save harmless the other party and its affiliates, their successors and assigns, their employees and agents and their heirs, legal representatives and assigns from all claims or demands whatsoever, including costs, expenses and reasonable attorney's fees incurred on account thereof, that may be made by damage to property or persons occasioned by acts or omissions of such party or its subcontractors, employees or agents or any of them arising in connection with their performance under this Agreement. Each of the parties will use its best efforts to insure that the employees comply with the other party's rules and regulations while on such party's premises.

The construction and performance of this Agreement will be governed by and constituted in accordance with the laws of the District of Columbia.

Neither party shall use the other party's name in marketing or advertising without providing an advanced copy to the other party and securing that party's consent in writing, which consent shall not be unreasonably withheld.

Neither of the parties shall be held responsible for any delay or failure in performance hereunder caused by fire, strikes, embargoes, requirements imposed by government regulations, civil or military authorities, acts of God or by the public enemy or other similar causes beyond such party's control.

No omission or delay in the part of either party of due and punctual fulfillment of any obligation shall be deemed to constitute a waiver by the other party of any of its rights to require such due and punctual fulfillment of any other obligation hereunder, whether similar or otherwise, or a waiver of any remedy it may have.

If any provision or provisions of this Agreement shall be held to be invalid, illegal or unenforceable, the validity, legality and enforceability of the remaining provisions shall not in any way be affected or impaired thereby.

This Agreement can only be modified by written agreement duly signed by persons authorized to sign such agreement on behalf of the parties.

If any legal claim or arbitration is brought or commenced by either party to this Agreement against the other for the enforcement of this Agreement or because of an alleged dispute, breach or default under this Agreement, the prevailing party shall be entitled to recover reasonable attorney's fees and other costs in such actions in addition to all other relief to which said party may be entitled.

This Agreement sets forth the entire agreement and understanding between parties as to the subject matter hereof and merges all prior discussions between them. Neither of the parties will be bound by any conditions, definitions, warranties, understandings, modification, or amendments except as expressly provided herein or as duly set forth on or subsequent to the effective date hereof in writing that specifically refers to this Agreement and that is signed by proper and duly authorized representatives of the party to be bound thereby.

Pintail Systems, Inc.	Hecla Mining, Inc.
_____	_____
David D. Gridley President	Todd Fayram Unit Manager
Date: _____	Date: _____

PROPOSAL

prepared for

HECLA MINING, INC.
YELLOW PINE UNIT

PILOT PLANT TEST PROGRAM

BIOTREATMENT OF CYANIDE IN HEAP LEACH SPENT ORE

COLUMN TEST DESIGN

PINTAIL Systems, Inc.
11801 E. 33rd Ave
Suite C
Aurora, CO 80010
(303) 367-8443

Spent Ore Bioremediation, Cyanide Biotreatment

Introduction

Mining operations at Hecla Mining's Yellow Pine Unit are reaching a point where it is appropriate to consider detoxification of the spent ore from the heap leach operations. The purpose of the work suggested in this proposal is to compare biotreatment, water washing and peroxide treatment of the ore. Data from column tests will be used in planning in Statement of Work for field treatment of spent ore cyanide detox. PSI has designed treatment bacteria populations that are balanced with cyanide oxidizing bacteria. A heap leach biodetox would be competitive with conventional treatment in time and material costs.

This proposal suggests a plan for column tests comparing peroxide treatment and water washes to bioremediation of spent ore. The parallel correlation of peroxide, water and bacteria washes will allow us to assess the feasibility of using biotreatment to decompose metal-cyanide compounds and nitrates in spent ore residue. Data from these tests will be used to complete a cost and engineering study for field spent ore detox.

A mix of PSI treatment bacteria proven in other applications will be adapted to the Hecla Yellow Pine spent ore and will be applied to spent ore in a series of column treatment tests. Six inch x ten foot PVC columns will be loaded with spent ore and will be leached with peroxide, bacteria or water. The application rates will be controlled and both the spent ore and column leachate solutions will be analyzed for total cyanide, weak acid dissociable cyanide and leachable metals.

Cyanide metabolism is known to occur in several species of bacteria. Bacteria that have the capacity for enzymatic hydrolysis of ionic cyanide or metallo-cyanide compounds use the carbon and/or nitrogen of the cyanide to meet nutritional needs of the cell. The end-products of cyanide metabolism are natural and non-toxic. Some of the reactions involved in microbial cyanide oxidation include:

1) $2Fe(CN)_6^{4-} + 29H_2O + 6.5O_2 \cdots\cdots> 12CO_3^{2-} + 12NH_3 + 2Fe(OH)_3(s) + 161$

2) $M_xCN_y + 2H_2O + 0.5O_2 \cdots\cdots> M/\text{bacteria} + HCO_3 + NH_3$

3) $NH_3 \cdots\cdots> NH_2OH \cdots\cdots> HNO? \cdots\cdots> NO_2 \cdots\cdots> NO_3$

4) $NO_3 \cdots\cdots> NO_2 \cdots\cdots> NO \cdots\cdots> N_2O \cdots\cdots> N_2$

5) CN + bacteria $\cdots\cdots>$ purines, pyrimidines, cyanohydrin, formaldehyde, etc.

Laboratory/Pilot Plant Workplan - Spent Ore Cyanide Biodecomposition

Task 1. Waste Characterization
At least 750 kg of fresh spent ore from cyanide leaching will be provided for the column tests. The spent ore will be blended and sampled for cyanide and metals analysis. At least ten split samples will be leached with 5% sodium hydroxide and distilled for WAD and total cyanide. A representative sample will also be extracted for leachable metals according to the TCLP leaching procedure. This phase of the test program would take approximately one week after receipt of the spent ore.

Task 2. Bacteria Adaptation to Spent Ore
The working population of bacteria will be grown in spent ore infusion broths to adapt to toxins and available nutrients. The cyanide and nitrogen in the spent ore will serve as the primary carbon and/or nitrogen source for bacteria nutrition. Other required trace nutrients will be provided in the chemically defined broths. This part of the test program should require one to two weeks after receipt of the spent ore.

Task 3. Biotreatment, Peroxide and Wash Column Parallel Treatment Tests
Blended, spent ore will be loaded into six each 6" x 10' PVC columns at a density of 95-100 lbs/ft^3. Each treatment will be modeled in at least two column tests to minimize sampling, analytical and treatment errors. A bacteria, peroxide, or water solution will be applied to each column at normal leach application rates (0.005 gpm/ft^2). Column effluent solutions and samples of the spent ore will be analyzed during the course of the test for cyanide and leachable metals. A material balance will be completed for each column at the completion of the test. A comparison analysis will show relative treatment efficiencies for each design with total pore volumes necessary for each treatment.

Task 4. Series Column Biotreatment Tests
Spent ore will be loaded into two of the 6" x 10' columns designated for biotreatment. Effluent solutions from the second biotreatment column in the Parallel Column Tests will be applied at the same application rates as the parallel column treatments. Effluent solutions from the first series biotreatment column will be applied to the second biotreatment column. The series column tests will provide data on bacteria activity at a total 30 foot spent ore depth. The overall column test concept is diagrammed in Figure 1.

Task 5. Data Evaluation and Scale-Up Cost Analysis
All solution and waste solids data will be evaluated and if biotreatment compares favorably a scale-up cost prediction will be made for larger field treatments. The final project report will summarize test data for leachate solution and spent ore analysis and will provide a material balance for each treatment. A diagram of the column test design is shown in Figure 2. The project timeline is presented in Figure 3.

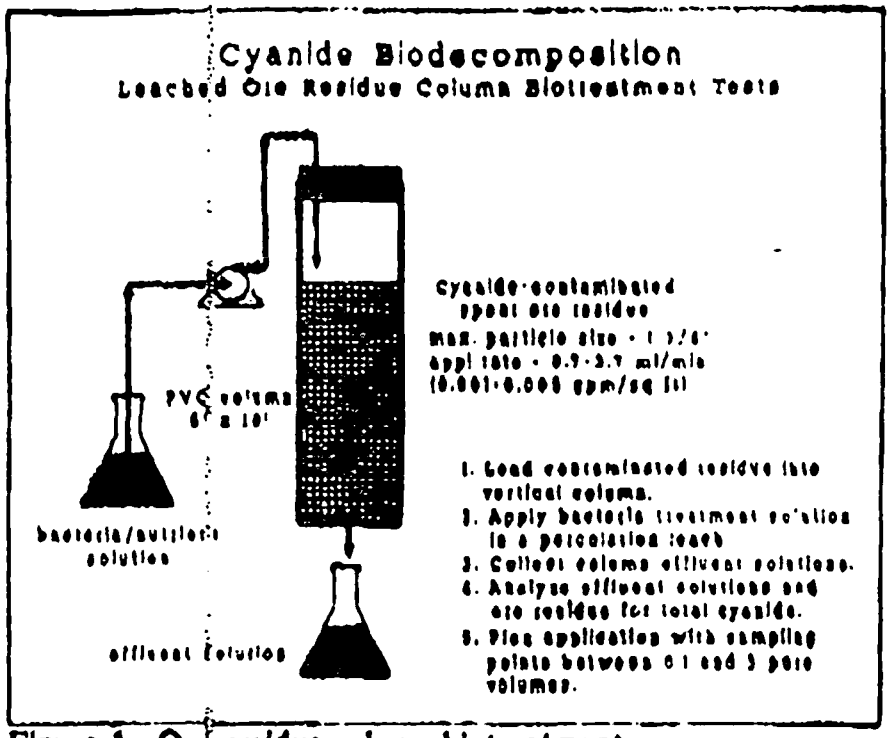

Figure 1. Ore residue column biotreatment

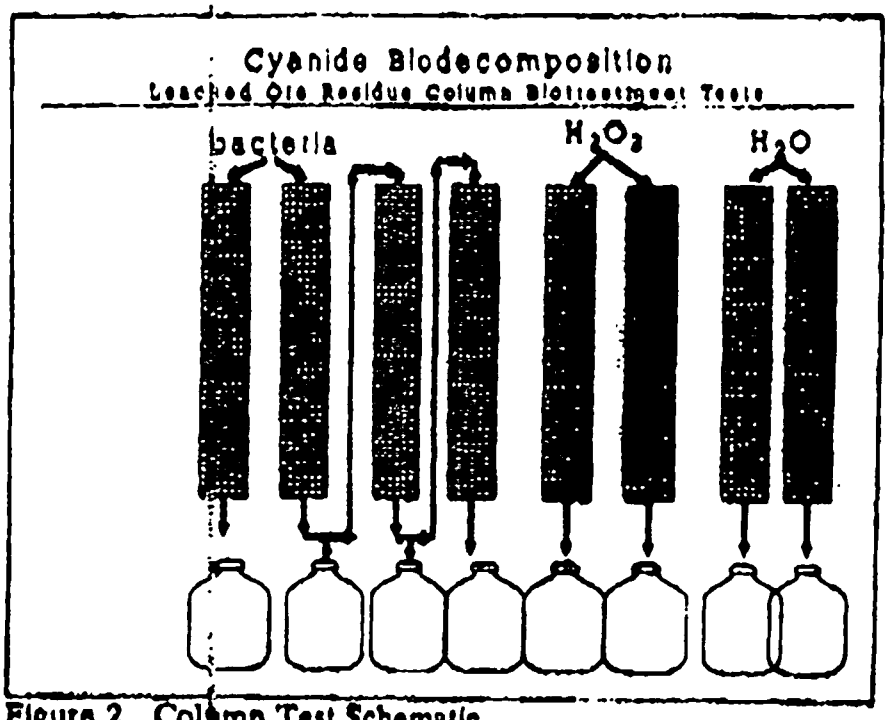

Figure 2. Column Test Schematic

Figure 3. Tentative Project Schedule

task no.	work description	start date	task duration (weeks)	end date	week number 1	2	3	4	5	6	7	8	9	10	11	12
	MAJOR MILESTONES		12		ATP					BPE				FTD		
	REPORT SCHEDULES						MP					MP				FPR
	AUTHORITY TO PROCEED	01-Nov-91	NA													
1	WASTE RECEIPT	04-Nov-91	NA													
2	WASTE CHARACTERIZATION	04-Nov-91	1	11-Nov-91												
3	CULTURE ADAPTATION/AUGMENTATION	04-Nov-91	2	18-Nov-91												
4	COLUMN TREATMENTS (PARALLEL):		4-5													
4a	2 EACH WATER WASH (W#1, W#2)	18-Nov-91	4	13-Dec-91												
4b	2 EACH PEROXIDE WASH (P#1, P#2)	18-Nov-91	3	06-Dec-91												
4c	2 EACH BIOTREATMENT (B#1, B#2)	18-Nov-91	2	29-Nov-91												
	IN-SERIES COLUMN ADD-ON:															
4d	2 EACH CONTINUOUS W/B#2 eff.	02-Dec-91	3	20-Dec-91												
5	DATA EVALUATION	23-Dec-91	2	03-Jan-92												
6	FINAL REPORT COMPILATION	06-Jan-92	2	17-Jan-92												

ATP = authority to proceed
MPR = monthly progress reports
FPR = final project report
BTE = biotreatment preliminary evaluation
FTD = field biotreatment test design

Cost Breakdown

Spent Ore Cyanide Bioremediation

Phase	Description	Cost
1	waste characterization	$575.00
2	biotreatment culture adaptation	$2485.00
3	column treatment tests	$16,600.00
4	data evaluation	$950.00
5	final report preparation	$2200.00
	TOTAL COST	$22810.00

Leaching.

DETOX AND TREATMENT
CONSULTING, INC.

7205 So. Chase Court
Littleton, CO 80123
303 972-0474

May 25, 1994

Mr. Martin Quick
Vice President - Operations
Dakota Mining
410 17th Street
Suite 2450
Denver, CO 80202

Dear Mr. Quick,

The use of substitutes of cyanide to extract precious metals has long been a subject that many companies have toyed with.

Cyanide, because of it public perception (used in executions and the "Tylenol Poisoning"), has long been the rallying point of environmentalists to take exception to precious metal projects. As regulatory agencies review present mining progress in light of minor and major containment failures, they find that although toxic, cyanide has at best an ephemeral existence outside processing conditions. When the pH level of the receiving solution is at natural conditions (pH 6.5 to 8.5), free cyanide is rapidly removed from solution by minimal aeration. Weak Acid Dissociable (WAD) complexes release free cyanide at rates low enough to either become used as a food source by flora and micro-biota or become off-gassed almost immediately. This is not to say that cyanide released to the environment is not potentially harmful, rather agencies are beginning "to know the enemy and fear it less". Other mine associated problems (nitrates, AM(R)D, etc.) appear to be more of a point of contention and require the operator's attention.

But no matter how accustomed the regulators become to cyanide, the public perception of cyanide can be a "sticking point" for potentially profitable projects. Therefore, alternate lixiviants may be the only route open in some cases. The alternative lixiviants for cyanide are:

1. Chlorine Oxidation
2. Bromide/Brominated Hydantoins (with Br_2)
3. Acidic Thiourea, Ferric Iron and Sulfur Dioxide
4. Thiosulfate/Copper/Ammonia

The key to any precious metal lixiviant is producing a chemical compound of gold or silver that is soluble under the aqueous conditions present in leaching. Most (if not all) leaching processes utilize complexation of the metal ions. The gold leaching chemistry utilizes complexes of both the aurous (Au^{+}) or auric (Au^{+3}) ions. Cyanide leaching produces aurous complexes as does thiourea ($CS(NH_2)_2$) and thiosulfate ($S_2O_3^{-2}$). The other methods involve significantly higher oxidizing states and produce auric complexes. Under most circumstances, silver complexes are formed from the argentous (Ag^{+}) rather than the argentic (Ag^{+2}) ion. A spectrochemical series of all ligands with one metal ion is:

$$I^- < Br^- < S^{-2} < SCN^- < Cl^- < OH^- < H_2O < NH_3 < CN^-$$

This series is abbreviated to drop ligands of little interest to the mining industry. This type of reactivity series should be used with caution, because it represents an over simplification of complexation chemistry. The strong complexes will result from compounds produced on the extreme right of the series and decrease in energy as you move to the left. The strength of the complex usually indicates the ease at which the complex is made, but this is not the only factor involved in the leaching and recovery process.

Chlorine

Using chlorine to leach gold is a very well known technology. The Miller process is used by most refineries (Handy & Harman, Johnson Mathney, etc.) to produce high purity metal (99.99% pure). Silver is insoluble in chloride solution except when sufficient excess chloride is present to produce complexed silver chloride ($AgCl_2^-$, $AgCl_4^{-3}$), which is soluble. The precious metal is recovered from solution by the same methods as cyanide complexes with similar loadings and kinetics. The toxicity of chlorine is extremely low (physiological saline contains 9000 ppm chloride). Chloride is more toxic to plant life than animal life, and therefore agricultural use determines the levels of acceptable chlorides in solution. The chlorine leaching utilizes various chlorine compounds from chlorine gas (Cl_2) to hypochlorite (OCl^-) to chlorate (ClO_3^-). Chlorine gas and hypochlorite have been used on refractory ore to consume carbonaceous material to oxidize some sulfides. Presently, many state regulators require a minimization of the amount of chlorides produced on site. The main reason is that throughout the West surface water is constantly acquiring chlorides from surface run-off, which causes extreme degradation of the agricultural water usage. Some states are using desalination processes to decrease the salt load in the waters of the state. Chloride removal technology is well known, but quite expensive. Additionally, all removal methods utilize the production of a brine that has to be disposed of in an environmentally safe manner (solid waste (non-hazardous) disposal or deep well injection). The chloride complex can be recovered using standard ion exchange resin technology, which is not the case with cyanide (due to resin poisoning)

Bromide/Brominated Hydantoins

Bromine leaching chemistry is being aggressively promoted in the industry as a safe cyanide alternative. The Geobrom™ products are halogen analogs of di-methyl hydantoin and in some cases free bromine. Bromide LD_{50}'s are 3500 mg/kg (for sodium bromide). The halogen analogs of di-methyl hydantoin and protonated (spent) di-

methyl hydantoin have LD_{50}'s of ~600 mg/kg and 7800 mg/kg, respectively. Bromine leaching is inhibited by the presence of oxidants.

Standard recovery methods (zinc precipitation and carbon adsorption) are effective for bromide solution. The optimum carbon absorption range is a pH level of 3-5. Bromide gold complexes are also recovered using ion exchange resins. The optimum pH range various with the individual resins used. Recovery from solution is via zinc or hydrazine precipitation.

Reviewing the literature, it appears that bromine absorbs onto carbon at the same levels as cyanide, but the kinetics appear to be slower. The slower kinetics may require more retention time in absorption columns.

Thiourea/Ferric/Sulfur Dioxide Leaching

The thiourea use has been contemplated for many years, but has yet to catch on in "Free World" countries. The use of SO_2 with ferric/thiourea leaching has been put forth by SKW Trostberg AG, of (West) Germany. This thiourea leaching method seems to have significantly higher kinetics than thiourea/ferric leaching. The SO_2 addition also allows significantly lower thiourea consumption, since the material does not degrade to cyanamide and native sulfur. The thiourea leaching process is an acidic leaching process that requires the presence of condensed phase oxidants (ferric iron compounds or hydrogen peroxide).

Unlike the previous anionic complexes, thiourea forms cationic complexes. The acidic, higher oxidation levels can allow enhanced recovery due to breakdown of gangue minerals, such as pyrite and arsenopyrite. The leaching kinetics of thiourea is significantly faster than cyanide leaching. Additionally, elevating leaching temperatures significantly increases leaching kinetics. Temperature adjustment for cyanide is not recommended, since the thermo-decomposition of cyanide to ammonia and carbon dioxide is increased with increasing temperature. Therefore, any gains in kinetics are lost due to reagent depletion.

The precious metals are recovered from the leach solution by activated charcoal or resins (strong acid cationic exchangers or thiol resins).

Thiourea LD_{50}'s are 125 mg/kg. Some of the degradation products of thiourea are ammonia, foramidine, cyanamide, sulfur, nitrate and sulfate. In the case of ammonia and nitrates, the degradation products are of more environmental concern that the reactants.

Thiosulfate/Copper/Ammonia Leaching

The use of thiosulfate ($S_2O_3^{-2}$) ion to leach precious metals dates back to 1858. This leaching process has the tendency to dissolve other heavy metal ions (i.e, copper, mercury, nickel, cobalt, lead cadmium, etc.), which can cause ancillary environmental problems. Recovery from the thiosulfate solution is accomplished by iron precipitation. Carbon absorption has low, slow absorption rates, which are not conducive to recovering the precious metals. Zinc precipitation works but removes copper also, which tends to reduce the leaching efficiency of the recycled solution. No mention of ion exchange resin recovery was mentioned, but it would seem that this method may also work effectively.

Thiosulfate has a LD_{50} of 7,500 mg/kg. The environmental problem with this leaching method is the production of sulfate (secondary drinking water release standard of 250 ppm) and the heavy metals liberated during leaching.

Copper/Ammonia/Cyanide Leaching

The use of copper, ammonia and cyanide with high copper ores is a viable low toxicity cyanide leaching method. This leaching method requires a pH in the 6.5 to 8.5 range. Copper ammonium cyanide complex becomes the oxidant in this reaction, eliminating the need to have dissolved oxygen present. The level of free cyanide in this solution is kept low (10-20 ppm). Since this method does not completely eliminate the use of cyanide it can not be considered an alternate to cyanide leaching, but this method can significantly lower the problems associated with free cyanide in solution.

When using this leaching method on an ore that requires agglomeration, polymer must be used to bind the ore rather than cement or lime. Since the pH level of this leach solution must be kept in the range where the tri cyano copper complex is the predominate species, cement agglomeration can not occur and some other binding system must be used. This method will usually lend itself more readily to a Merrill-Crowe recovery system than carbon. When using carbon with copper/ammonia/cyanide, the tri cyano copper complexes load on the carbon displacing gold and silver. The resulting precious metal loading on the carbon is in the 30 - 50 ounce per ton range, which would require large stripping capacities (2-5 tons per day for 80 - 200 ounce per day operations).

This review is only a cursory look at the various leaching and recovery processes that can be used to replace cyanide. Hopefully, this review will give you an idea of the different alternatives. If you have a need for these types of processes, this will allow

you to start your search. When considering an alternate leaching system, look at the chlorine system first. After that, screen the other systems to determine which alternative method is most amenable to your ore. This review is not an all inclusive review of alternative lixiviants, but a review of technologies that have a chance to replace cyanide. Other potential lixiviants are iodine, malononitrile and aqua regia.

If you have any questions, please call me any time.

Sincerely,

Michael Drozd

Agglomeration with Pulp

A Concept to Improve the Economics of Heap Leaching

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Rod MacLeod / Laura Ramon

(From Jody Kelso at Cambrian).

INTRODUCTION

The advantages of using agglomeration in many heap-leaching applications have been well documented.[1]

This paper presents the concept of agglomeration with ground pulp, which will improve the overall extraction of gold at some heap-leach operations. The advantages are discussed together with situations in which this concept could be applied. Also, laboratory test results from three separate projects are briefly reviewed.

DETAILED DESCRIPTION

A typical agglomeration circuit is shown in Figure 1. Ore is crushed using two-stage crushing to a nominal minus 3/4 inch and fed to a stockpile.

Cement and cyanide, together with barren solution, are then added to the ore as it is fed at a steady rate from the stockpile into an agglomerator. Cement and moisture content are controlled to form stable agglomerates which are then fed to heaps for curing and leaching. There are many variations to this basic circuit, but in general, ore is crushed to the optimum size, balancing crushing costs and gold extraction; and moisture and a binder are added to form stable agglomerates.

The idea presented in this paper adds a small ancillary circuit to a basic agglomeration circuit. This addition can be as simple or as complicated as the economics of the situation dictate.

Figure 2 shows a basic agglomeration circuit modified with the addition of a small tertiary crusher, ball mill, and thickener. This circuit is used to take a bleed stream of crushed ore, preferably with the highest grade available, and grind it to a pulp. The pulp, with or without thickening, is then used to agglomerate the main stream of ore from the crusher stockpile. It has been well established[2,3] that the amount of fines present in the ore do not affect the ability to agglomerate, but moisture content is critical to producing stable agglomerates. Therefore, the amount of pulp used is dictated by moisture required for agglomeration of the crushed lower-grade ore. It follows that if only a small percentage (<15%) of high-grade pulp is available, the cyclone-overflow stream could be used directly in the agglomeration circuit. If a higher percentage of the ore is fed through the milling circuit, it may be necessary to reduce the moisture content of the pulp by thickening before it is added to the agglomerator.

Many other options are available, such as the use of wet crushing, open-circuit rod milling, gravity traps, etc., provided moisture in the final bleed-stream pulp does not exceed moisture required to agglomerate the rest of the ore.

APPLICATION OF THE CONCEPT

The concept was developed to optimize gold extraction from a satellite ore body near our Brewer Mine in South Carolina, and reference was first made to this idea in a February 1989 paper[4]. The satellite ore did not respond well to heap leaching, and there were insufficient grade and tonnage to justify the installation of a mill facility. By supplementing our main Brewer ore with ±20 percent by weight satellite ore ground to minus 100 mesh, we found the economics of the satellite ore body were greatly enhanced. Unfortunately, in the final analysis, the overall grade of the ore body was lower than originally projected which adversely affected the economics.

As well as satellite ore bodies which may exhibit different metallurgical characteristics, some ore bodies have distinct high-grade zones which can be separated during mining. If these are too small to justify the construction of a CIP/CIL plant, the concept presented here can be used to optimize extraction from the high-grade zones.

Finally, there are a number of conventional plants that have supplementary

heap-leach operations to treat the low-grade ore. Most of these plants are operating at maximum mill capacity which often reduces leaching time available and, therefore, reduces extraction efficiency. If excess milled pulp is diverted from the plant and used to agglomerate the ore in the heap-leach operations, leach time in the plant can be maintained to give optimum extraction and the heap-leach operation is improved at the same time.

ADVANTAGES

There are several advantages to agglomerating with pulp in the right applications.

- Significantly more gold can be extracted from milled ore. By selecting the high-grade areas, therefore, overall gold extraction is improved for only a small increase in capital.
- Laboratory tests completed to date indicate agglomerates formed with pulp are more stable and have improved permeability. This improvement enhances the rate of both precious-metal extraction and rinsibility after leaching.
- For small high-grade deposits with a halo of low-grade ore, precious-metal recoveries equivalent to conventional plants can be achieved without the expense of the installation of a CIP or CIL plant or the requirement and environmental problems of a separate tailings disposal area.
- If coarse gold is present in the high-grade portion of the ore body, a gravity trap can be installed in the milling circuit to remove the gold before it gets to the heaps where it would require longer leaching times for dissolution.
- The milling circuit is supplemental to the main crushing and agglomeration circuit and, therefore, can be taken out of service for maintenance and repair without impacting the whole operation.
- Gold extraction is accelerated and, therefore, cash flow is generated more quickly. Also, the pulp is in contact with a leach solution significantly longer than in a conventional mill, and extraction is therefore maximized.

LABORATORY TEST RESULTS

Three relevant metallurgical test programs have been completed at McClelland Laboratories in the last year.

Project 1: This ore from a Brewer Mine satellite ore body was comprised of quartzites and/or quartz schists with free gold in microshears and gold also encapsulated in coarse pyrite. The average head grade was approximately 0.07 oz Au/ton. Bottle-roll tests run for 96 hours on this ore gave the following results:

Particle Size (80% Passing)	Extraction %, Au
1/2"	44.2
1/4"	52.4
10 mesh	61.6
28 mesh	70.1
48 mesh	72.3
100 mesh	76.4

From these results, it was apparent that by grinding to 80 percent minus 100 mesh, gold extraction could be increased by approximately 25 percent. Agglomerates made using this pulp with minus 3/4-inch Brewer Mine ore exhibited good strength and permeability.

Project 2: The tested ore samples were comprised of basalt, tuff, and rhyolite. The tuff and rhyolite were more amenable to heap leaching than the basalt. High-grade ore is found in quartz veins throughout the deposit. Twelve percent of the total ore was high grade and could be mined and stockpiled separately.

Results of 96-hour bottle-roll tests on the high-grade material are shown below. The average head grade was around 0.2 oz Au/ton.

Particle Size (80% Passing)	Extraction %, Au
10 mesh	37.3
20 mesh	48.7
35 mesh	63.9
65 mesh	75.5
100 mesh	86.8
150 mesh	86.1
325 mesh	89.1

From these results it was decided to use an 80 percent minus 100 mesh high-grade pulp to agglomerate the low-grade ore at minus 3/4 inch in size.

Project 3: The ore samples evaluated were comprised of low-grade ore grading approximately 0.055 oz Au/ton and separate high-grade ore averaging approximately 0.12 oz Au/ton. The high-grade portion of the ore body was approximately 22 weight percent and contained visible gold.

Bottle-roll and column tests indicated that at an 80 percent minus 3/8-inch crush size, 65 percent gold extraction could be achieved. When the high-grade ore was ground to 80 percent minus 100 mesh, the gold extraction in a 72-hour bottle-roll test was 99 percent. It was decided, therefore, to

agglomerate the low-grade material with the high-grade pulp at 80 percent minus 100 mesh. A gold recovery of 77 percent was achieved from the combined pulp/crushed ore agglomerated feed in 44 days of column leaching and washing.

CONCLUSION

The concept of using pulp for agglomeration has been presented here. This technique is not suitable for all ore bodies, however, it should be considered when evaluating ore bodies for development using agglomeration and heap leaching.

REFERENCES

[1]McClelland, G.E. and Pool, D.L. and Eisele, J.A. (1983). "Agglomeration - Heap Leaching Operations in the Precious Metals Industry". Bureau of Mines Information Circular.

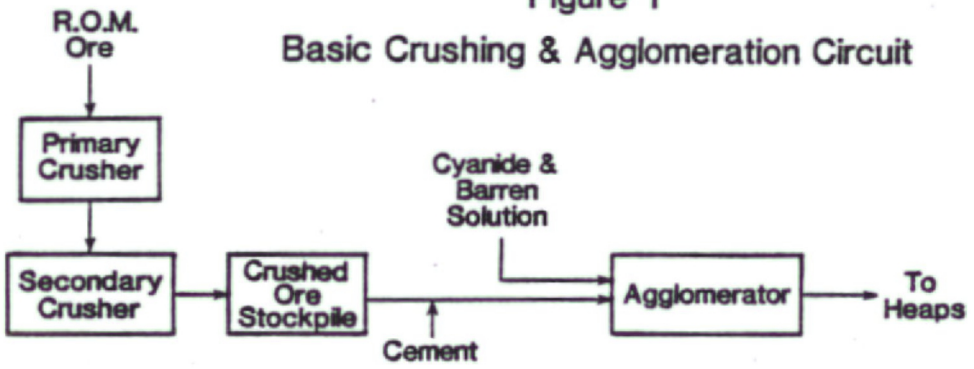
[2]Heinen, H.J. and McClelland, G.E. and Lindstrom, R.E. (1979). "Enhancing Percolation Rates in Heap Leaching of Gold and Silver Ores". Bureau of Mines Report of Investigation.

[3]McClelland, G.E. and Eisele, J.A. (1982). "Improvements in Heap Leaching to Recover Silver and Gold from Low-Grade Resources". Bureau of Mines Report of Investigation.

[4]McGregor, R.J. and Drozd, M.A. (1989). "Development and Start-Up of Precious Metal (Gold/Silver) Projects, Proc. Precious Metals' 89, Las Vegas, NV, February 1989

Figure 1

Basic Crushing & Agglomeration Circuit



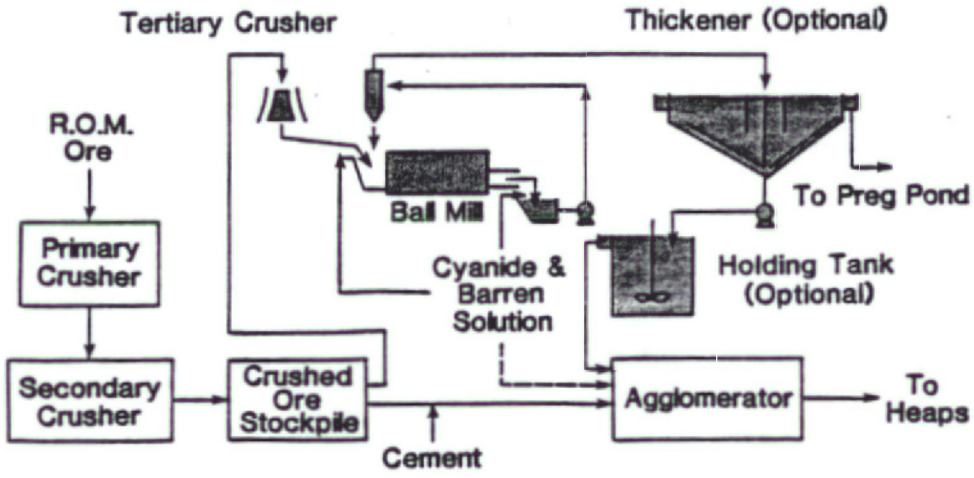


Figure 2 Modified Crushing & Agglomeration Circuit

MEMORANDUM

DATE: JULY 22, 1992

TO: MARTIN QUICK

FROM: JIM BARRON

SUBJECT: GOLD RECOVERY - LATEST VIEW

A constant concern of ours is the accurate assessment of monthly gold production. Our ability to make such predictions is not only based on accurate estimates of overall gold recovery but also is critically related to trying to predict the rate at which the recoverable gold will be leached.

Many factors must be considered in making these predictions and a project history file is most useful when attempting to make future estimates. Unfortunately two major parameters critical to making reliable production forcast have changed recently.

First, the ore material is different. It is more refractory than most of the material mined thus far in this projects history. Because we have virtually no test data regarding gold recovery from this material at the current crush size, we are forced to make gold production projections based on information we are gathering right now.

Second, our leaching rate history is limited to average leaching times of approximately 60 days. This of course is a consequence of our on-load, off-load operating system of leaching. The combination of these two factors makes the task of accurate production calculations analogous to flying blind in a fog at night, i.e. prediction of problems is impossible but you'll know immediately when disaster befalls you.

Currently we are compiling leaching rate information on cells for which leaching times are now in excess of 60 days. Four cells, or portions thereof, have been under leach for 90 days or more. Attached is a crude graph showing the percentage of recoverable gold leached through time (assuming a 55% overall gold recovery). The numbers 1, 2, 3, 6 and 7 correspond to the individual cells under leach and show their respective gold recovery at 30-day intervals.

The table below compares the average actual leach rate for all cells to the leach rate schedule used in the latest view forecast (Forecast 3-A). As shown here, it would appear that our "3-A" forecast is conservative in the first few months of leaching, but probably too liberal in the latter months, especially beyond 6 months (180 days).

LEACH RATE SCHEDULE OF RECOVERABLE OUNCES

MONTH

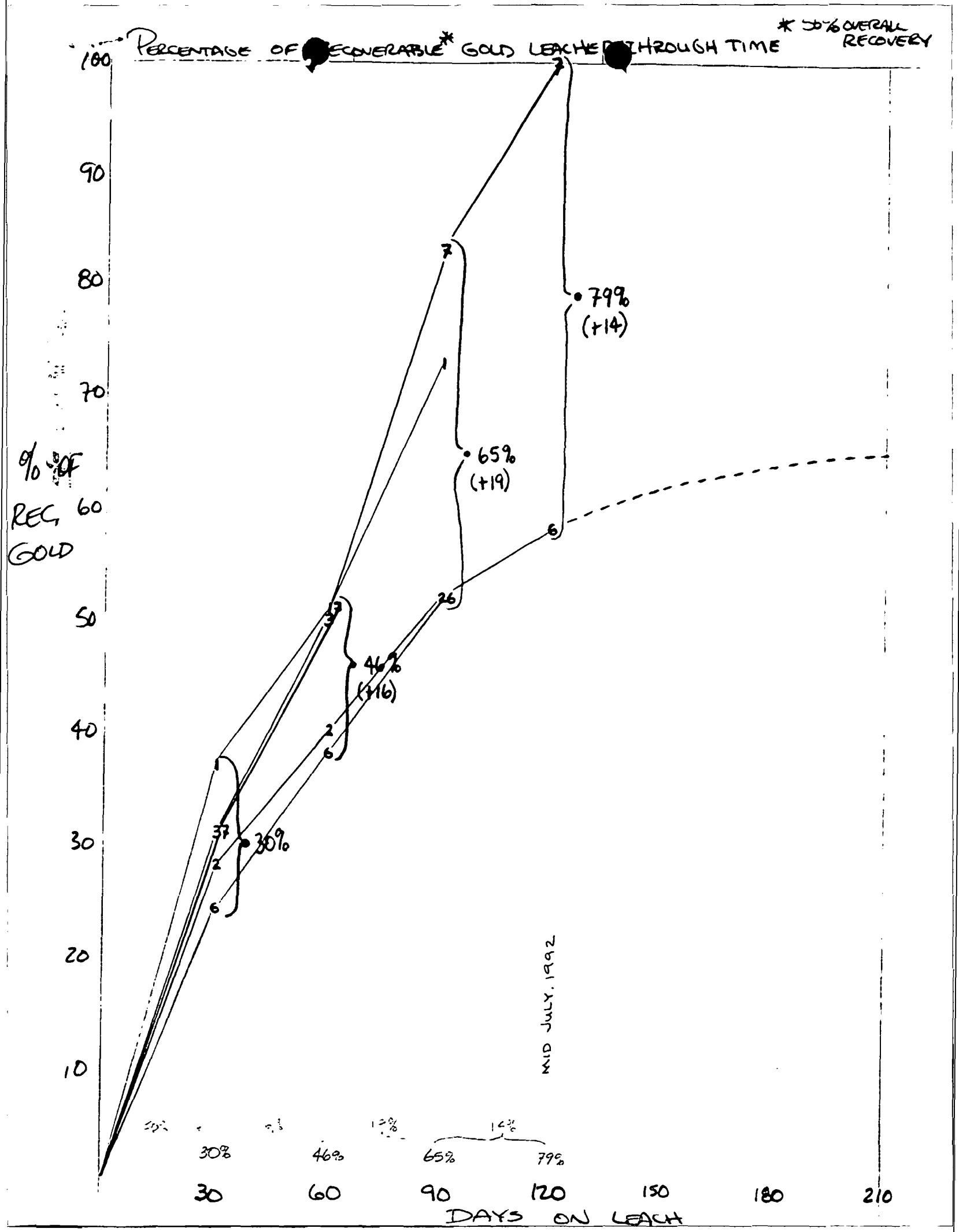
	1	2	3	4	5	6	7	8	9	10	11	12
3-A Forecast	15%	16%	16%	13%	11%	8%	7%	5%	3%	2%	2%	2%
(cumulative)	(15)	(31)	(47)	(60)	(71)	(79)	(86)	(91)	(94)	(96)	(98)	(100)
Average Actual	30%	16%	19%	14%	?	----						
(cumulative)	(30)	(46)	(65)	(79)	?	----						

As a more conservative approach I recommend we look more toward Cell #6 as the norm for future leaching rates because of its refractory nature. The actual leaching rate for Cell #6 is compared below to that of the 3-A forecast.

	1	2	3	4	5	6	7	8	9	10	11	12
3-A Forecast	15%	16%	16%	13%	11%	8%	7%	5%	3%	2%	2%	2%
Cumulative %	(15)	(31)	(47)	(60)	(71)	(79)	(86)	(91)	(94)	(96)	(98)	(100)
Cell #6	24%	14%	14%	6%	4%	2%	1%	1%	1%	1%	1%	1%
Cumulative %	(24)	(38)	(52)	(58)	(62)	(64)	(65)	(66)	(67)	(68)	(69)	(70)

What this means is that the process of leaching beyond 6 months is unacceptably overestimated in our current 3-A Forecast and should be recalculated based on the above leach rates in order to more accurately predict monthly gold production. I will run another forecast incorporating amore conservative leaching rate in months 6 through 12.

/pls


PERCENTAGE OF RECOVERABLE* GOLD LEACHED THROUGH TIME
* 50% OVERALL RECOVERY
% OF REC. GOLD
100
90
80
70
60
50
40
30
20
10
79%
(+14)
65%
(+19)
46%
(+16)
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MID JULY, 1992
30%
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DAYS ON LEACH